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CONTROL OF THE URETHANE CURE REACTION WITH SOLID
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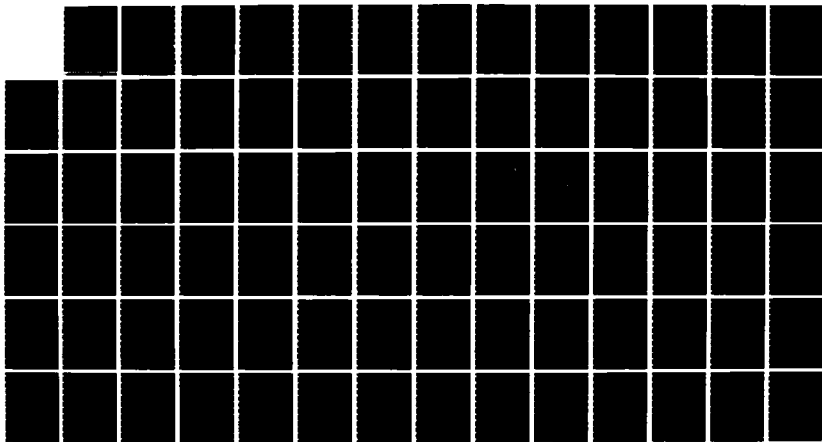
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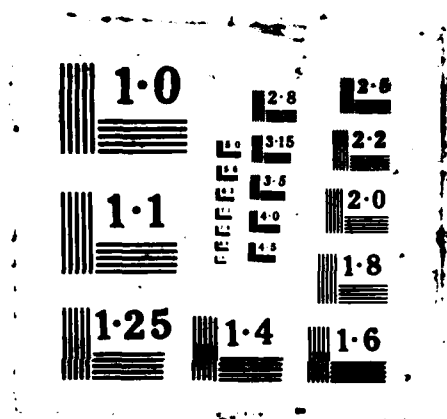
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TECHNICAL REPORT RK-

U-86-06

CONTROL OF THE URETHANE CURE REACTION WITH SOLID, BLOCKED ISOCYANATES

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FINAL REPORT

MORTON THIOKOL INC.

Huntsville Division

Huntsville, Alabama 35807-7501

PREPARED FOR:

Air Force Office of Scientific Research
Department of the Air Force

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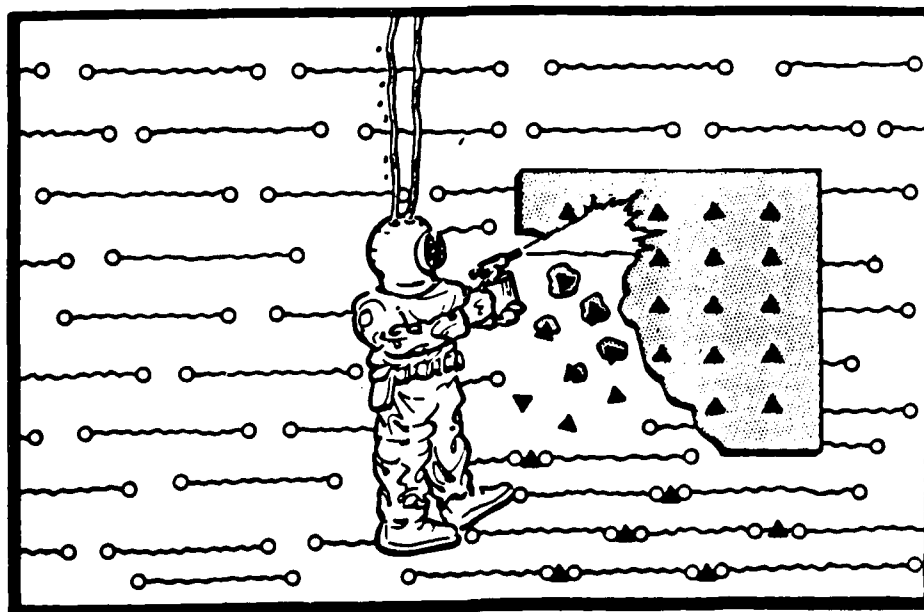
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MATTHEW J. KETTER

Chief, Technical Information Division

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FOREWORD

This is the final report for the program, "Control of the Urethane Cure Reaction with Solid, Blocked Isocyanates", submitted by Morton Thiokol, Inc./Huntsville Division to the Air Force Office of Scientific Research, Department of the Air Force, Bolling Air Force Base, D.C. 20332, in fulfillment of Contract F49620-84-C-0059.

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The following Morton Thiokol, Inc. personnel made significant contributions to this effort: Dr. W. H. Graham, Principal Investigator; Mr. R. E. Boothe and Ms. I. G. Shepard (retired), chemical synthesis; and, Mr. J. W. Blanks, chemical analyses.

Anthony J. Matuszko
Program Manager

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polymers and plasticizers was investigated. In Task 3 cure studies were performed, and the effect of particle size, catalysts and temperature on cure time and quality was investigated. Several solid, blocked isocyanates were evaluated in common liner and propellant formulations.

Accomplishments of this project included: (1) A catalog of 25 solid, blocked isocyanates prepared including x-ray studies, IR analysis, differential scanning calorimetry and particle size analyses, (2) Cures demonstrated in both carbon filled and non-carbon filled gumstocks, and with blocked isocyanates of varying melting points and structures, (3) Demonstration that gumstocks held at 5°C below the melting point of the blocked isocyanate do not cure, but rapid curing occurs when the temperature is raised above the "trigger" temperature, (4) solubilities of candidate blocked isocyanates were examined in common urethane forming polymers and plasticizers, (5) cure rates were compared in catalyzed and non-catalyzed gumstocks, (6) rapid cures were demonstrated at 145°F in a common liner formulation which did not cure at 130°F, and (7) cures were demonstrated at 145°F in two standard propellant formulations.

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Anthony J. Matuszko
Program Manager

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SUMMARY

Controlling the profile of the hydroxyl/isocyanate cure reaction remains a challenge which has practical implications in the many areas of application of polyurethane materials. It is desirable that the processing time or potlife be extended, while limiting the required cure time and/or temperature. These contradictory requirements necessitate unusual techniques, since the same NCO/OH reaction which is responsible for limiting molecular weight and viscosity also produces the ultimate cure.

The objectives of this program are to demonstrate that solid, blocked isocyanates can control the urethane cure reaction by providing indefinite potlife below the melting point of the solid, and a rapid, controllable cure above the melting point. More generally, the approach addresses the question of differences in reactivity of molecules in solution and in the solid state. The relationship of melting temperature, solubility in the binder and particle size of the blocked isocyanate as it relates to polyurethane chemistry is also investigated.

This program is divided into three tasks. Task 1 was concerned with synthesizing a group of solid, blocked isocyanates with various melting temperatures, and preparing a catalog of cure agents/"trigger" temperatures. The crystallinity of the compounds was also determined. In Task 2 the solid, blocked isocyanates were examined by infrared spectroscopy, and the solubility of candidate compounds in common urethane forming polymers and plasticizers was investigated. In Task 3 cure studies were performed, and the effect of particle size, catalysts and temperature on cure time and quality was investigated. Several solid, blocked isocyanates were evaluated in common liner and propellant formulations.

Accomplishments of this project include:

- A catalog of 25 solid, blocked isocyanates was prepared and x-ray studies, IR analyses, differential scanning calorimetry and particle size analyses were performed.
- Cures were demonstrated in both carbon filled and non-carbon filled gumstocks, with blocked isocyanates of varying melting points and structures.
- Established that gumstocks held at 5°C below the melting point of the blocked isocyanate do not cure, but rapid curing occurs when the temperature is raised above the "trigger" temperature.
- Examined solubilities of candidate blocked isocyanates in common urethane forming polymers and plasticizers.
- Compared cure rates in catalyzed and non-catalyzed gumstocks
- Demonstrate rapid cures at 145°F in a common liner formulation which did not cure at 130°F
- Demonstrated cures at 145°F in two standard propellant formulations

TABLE OF CONTENTS

	<u>Page</u>
Foreword	
DD Form 1473	
Summary	1
Table of Contents	2
List of Tables	3
List of Figures	4
1.0 <u>INTRODUCTION</u>	5
1.1 Background	5
1.2 Objectives	5
1.3 Scope of Program	7
1.4 Approach and Organization of Experimental Effort	7
1.5 Organization of Report	10
1.6 References	10
1.7 Personnel	12
2.0 <u>KEY FINDINGS AND ACCOMPLISHMENTS</u>	12
3.0 <u>SYNOPSIS OF TASK 1</u>	14
3.1 General	14
3.2 Synthesis of Blocked Isocyanates	14
3.3 X-Ray Studies	14
3.4 DSC Analysis	19
4.0 <u>SYNOPSIS OF TASK 2</u>	19
4.1 General	19
4.2 Infrared Analysis	19
4.3 Solubility Studies	23
5.0 <u>SYNOPSIS OF TASK 3</u>	25
5.1 General	25
5.2 Cure Studies	25
5.2.1 Non-Carbon Filled Gumstocks	25
5.2.2 Carbon-Filled Gumstocks	25
5.2.3 Cure Profiles	27
5.2.4 Gumstocks With Mixtures of Blocked and Unblocked Isocyanates	27
5.3 Effect of Added Cure Catalysts	29
5.4 Effect of Blocked Isocyanate Particle Size on Cure Quality	29
5.5 Liner Formulations	34
5.6 Propellant Formulations	34
6.0 <u>CONCLUSIONS AND RECOMMENDATIONS</u>	36
<u>APPENDICES</u>	
Appendix A - Synthesis of Blocked Isocyanates	39
Appendix B - Representative DSC Traces	41
Appendix C - Infrared Spectra of Blocked Isocyanates	48
Appendix D - Non-Carbon Filled Gumstocks	73
Appendix E - Carbon Filled Gumstocks	75

LIST OF TABLES

<u>TABLE</u> <u>NO.</u>		<u>PAGE</u> <u>NO.</u>
3.0-1	A List of Compounds and Their Structures Used In The Synthesis of Solid, Blocked Isocyanates	15
3.0-2	List of Prepared Solid, Blocked Isocyanates	18
4.0-1	Solubility Studies	24
5.0-1	Blocked Isocyanates Used in Preparing Non-Carbon Filled Gumstocks	26
5.0-2	Blocked Isocyanates Used in Preparing Carbon Filled Gumstocks	26
5.0-3	Cure Profiles of Carbon Filled Gumstocks	28
5.0-4	Cure Profiles of Gumstocks Prepared With TDI Liquid and TDI/2-NP	28
5.0-5	Results of Particle Size Measurements	33
5.0-6	Results of Cures With Blocked Isocyanates of Various Particle Sizes	33
5.0-7	Results of Liner Formulations	35

LIST OF FIGURES

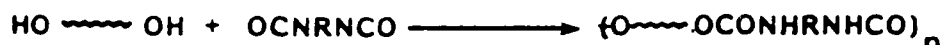
<u>FIGURE NO.</u>		<u>PAGE NO.</u>
1.0-1	Overview of Blocked Isocyanate Program	8
1.0-2	Control of the Urethane Cure Reaction With Solid Blocked Isocyanates	11
3.0-1	Several Typical Blocking Reactions	17
3.0-2	Examples of Typical DSC Plots	20
4.0-1	IR Spectrum Showing NCO and NHCO_2 Peaks	21
4.0-2	Unblocking of Mono-blocked TDI/2-NP	22
5.0-1	IR Spectrum of R45M/AO and TDI/2,4-DNP at Room Temperature	30
5.0-2	TDI/2,4-DNP and R45M/AO, DBTDL Added, 2 Hours at 65°C	31
5.0-3	TDI/2,4-DNP and R45M/AO, No DBTDL, 2 Hours at 65°C	32
5.0-4	ATR Infrared Spectrum of Uncured Propellant	37

1.0 INTRODUCTION

1.1 BACKGROUND

Polyurethanes, the product of the reaction of polyfunctional alcohols and polyfunctional isocyanates, are widely used and versatile polymeric materials. Reasons for the widespread use of polyurethanes include: (1) excellent compatibility and stability, (2) ease of processing, (3) good physical characteristics and tensile properties, (4) lack of by-product formation during cure, and (5) the wide variety of commercially available polyfunctional isocyanates and alcohols which are useful as starting materials. These characteristics of polyurethanes have resulted in their use as binder materials in filled and unfilled elastomers, as engineering plastics, as fabric modifiers, in paints and coatings, and in foamed applications. However, in certain applications, constraints imposed by temperature and other processing considerations provide obstacles to the economical use of polyurethanes. This is especially true in highly filled, temperature sensitive systems such as rocket and gun propellants and adhesives.

Controlling the profile of the hydroxyl/isocyanate cure reaction remains a challenge which has practical implications in the many areas of application of polyurethane materials. In many of these applications it is desirable that the processing time or potlife be extended while limiting the required cure time and/or temperature. These contradictory requirements necessitate unusual techniques since the same NCO/OH reaction which is responsible for limiting molecular weight and viscosity increase also produces the ultimate cure.



Approaches which have been examined for controlling potlife and cure time at Morton Thiokol Inc./Huntsville include:

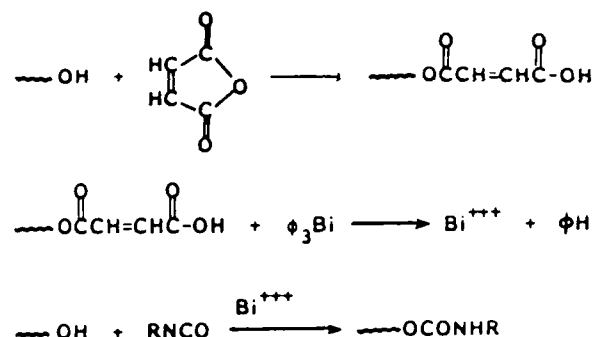
- Isocyanate cure agent selection and choice of processing/cure temperatures
- Delayed quick cure; designed to greatly shorten propellant cure time without producing prohibitively short potlife.
- Blocked isocyanate cure agents for providing long potlife and short to normal cure times.

The initial efforts to control propellant potlife and cure times involved trade-off studies using different cure agents such as TDI, HMDI, IPDI, Desmodur-100, PAPI, etc. Usually, IPDI was selected because, at maximum standard processing/cure temperatures of 135°F to 170°F, this isocyanate most nearly matched an acceptable cure profile. If cure times were excessively long, the usual remedy was to cure near 170°F or add low levels of relatively weak cure catalysts.

A major advance in cure control chemistry was the introduction of the three component (triphenyl bismuth, maleic anhydride, and magnesium oxide) "delayed quick cure" (DQC) catalyst system, which usually provided five to

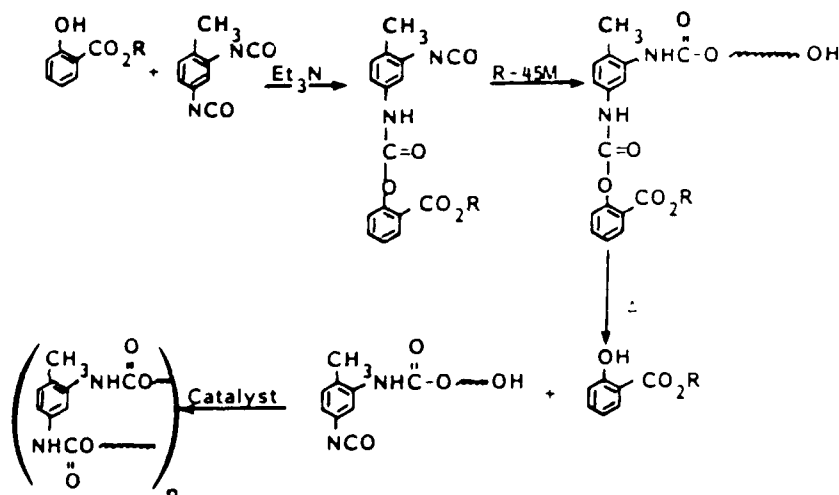
ten-fold shortening of cure times and only up to a two-fold decrease in potlife. This work, initiated under IR&D programs¹, was demonstrated in an Army program². Both conventional and minimum smoke propellant and liner mechanical properties are ordinarily enhanced by the DQC catalyst with equivalent or superior properties being attained at lower ratios of isocyanate to hydroxyl. Ordinarily, only 0.025% of each of the three components is used, but some fine-tuning of the cure profile can be achieved by variations of the level of each of the components. Later, Atlantic Research Corporation reported³ the use of the Morton Thiokol, Inc. catalyst system in high temperature cures. Morton Thiokol, Inc. has shown that the DQC was applicable to liner systems in two Air Force Rocket Propulsion Laboratory-funded programs⁴.

The delayed quick cure catalyst system depends upon the generation of an active cure catalyst from the reaction of maleic anhydride with polymer hydroxyl groups. The magnesium oxide scavenges stray acid which may be present prior to the desired generation from maleic anhydride. The equations involved are:



Details of the mechanism and scope of the reaction have been provided by Sinclair⁵.

The third cure profile control approach developed at Morton Thiokol/Huntsville involves the use of salicylate esters as isocyanate blocking agents. Again, the concept has been demonstrated in both propellant⁶ and liner⁷ systems. The advantage of the salicylate blocked isocyanate method is that very long potlife can be achieved at convenient processing temperatures and cure times can be controlled by the type and level of cure catalyst used. The cure scheme using a soluble salicylate ester blocked isocyanate is illustrated below:



An excellent review of blocked isocyanates and their applications has been provided by Wicks⁸. Included in this article is information on structure versus unblocking temperature.

1.2 OBJECTIVES

The objective of the program discussed in this report is to demonstrate that insoluble, solid blocked isocyanates will initiate cure of polyfunctional alcohols only above their melting points, thus providing indefinite potlife below the melting point of the solid, and a rapid, controllable cure above the "trigger" temperature. A blocked isocyanate is one that has been reacted with a material which prevents its reaction at lower temperatures, but allows reaction at elevated temperatures. This allows for "master batching" of the total binder and storage at ambient temperatures or lower for prolonged periods of time. In addition, the relationship of melting temperature, solubility in binder, molecular structure, and particle size of the blocked isocyanate is determined as it relates to polyurethane chemistry.

1.3 SCOPE OF PROGRAM

The technical scope of this program is to demonstrate the viability of solid, blocked isocyanates to provide a controllable urethane cure only above their melting point. The overall program was divided into 3 tasks. The flow of technical information and logic is shown in Figure 1.0-1.

The first task of the program, Synthesis of Solid, Blocked Isocyanates: Catalog of Cure Agents/Trigger Temperatures, was designed to provide a series of solid, blocked isocyanates with a range of melting points from the reaction of phenols of various structures with difunctional isocyanates. Each of the cure agents was further characterized by x-ray scanning measurements to determine their crystallinity. From these data a catalog of cure agents and melting points was prepared.

The second task of the program, Characterization and Comparison of Solid, Blocked Isocyanate Candidates, was designed to determine the structures of the cure agents, and to measure the solubilities of candidate blocked isocyanates in typical urethane forming polymers and plasticizers with a broad range of polarities. The results of these measurements were examined for possible correlation between blocked isocyanate structural features and solubility.

The third task of the program, Cure Studies: Influence of Temperature, Particle Size, and Catalyst Content, was designed to demonstrate cures in several temperatures ranges. Also examined was the correlation between the trigger temperature of the cure reaction and the melting point of the cure agent. The effect of added cure catalyst was examined, and cure profiles were measured. The effect of particle size was also investigated, and cures were demonstrated in several liner and propellant formulations.

1.4 APPROACH AND ORGANIZATION OF EXPERIMENTAL EFFORT

The theoretical basis upon which this program lies is that crystalline and dissolved materials exhibit different reactivity. The reactivity of most compounds is greatly inhibited in the crystalline state because crystal lattice energy lowers the free energy of the individual molecules. Examples of this phenomenon are: (1) the commonplace decomposition of unstable materials at

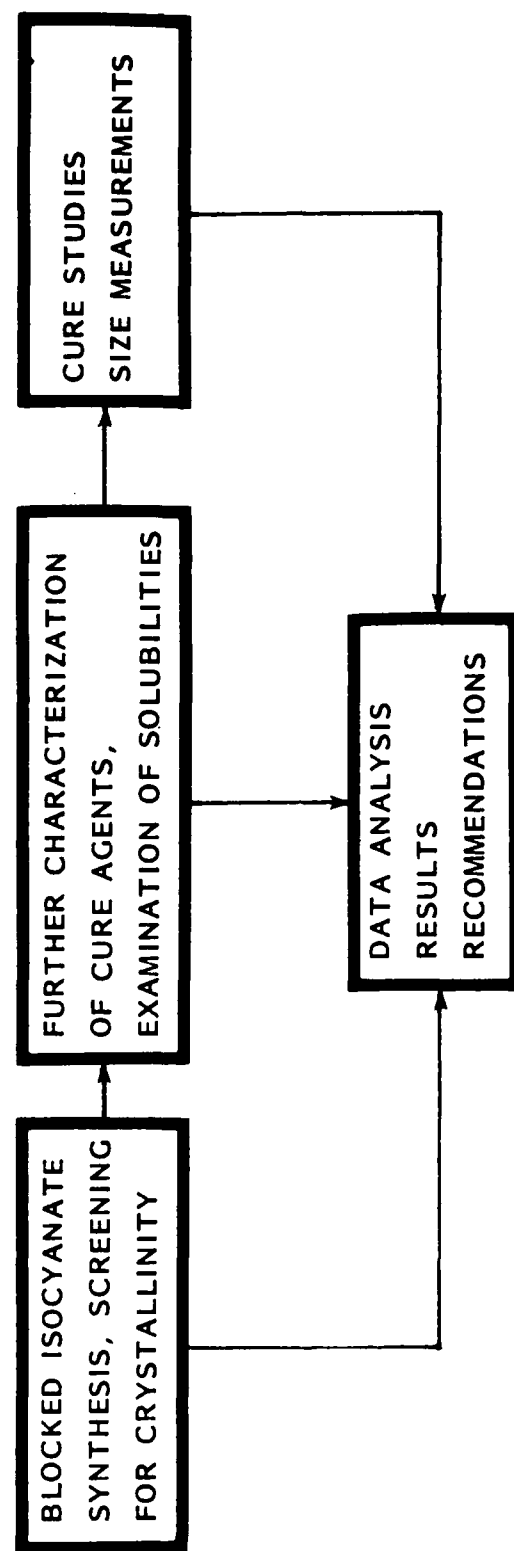


Figure 1.0-1. Overview of Blocked Isocyanate Program.

their melting points even though the melting points are substantially above the decomposition temperature of the same compound in solution (the decomposition exotherm of HMX at its melting point and at a substantially higher temperature than that of RDX, with which it is structurally very similar, is a specific example), (2) unimolecular decomposition reactions of diacetyl peroxides and azo compounds are also slow or unobservable in the solid state, in spite of the fact that the formation of CO_2 or N_2 renders these reactions irreversible, (3) the mutarotation of an optically active biphenyl ion at 100°C in solution takes place in a few hours, but does not proceed to a measurable extent in 55 days in the crystalline state at the same temperature⁹. The key factor for the success of this method is that the solid, finely divided, crystalline, insoluble blocked isocyanates remain blocked below their melting point, but dissociate readily above their melting point. In order to achieve a satisfactory cure, it is necessary that the blocked isocyanate cure agents be finely divided solids which are insoluble in the binder medium. After melting and dissociation of the blocked isocyanates into the reactive, free isocyanate, it is necessary that the latter material be soluble in and diffuse readily throughout the binder phase.

Task 1 was organized to provide a variety of solid, blocked isocyanates with various melting points from which to choose. This range of melting points provides a corresponding range of potential "trigger" cure temperatures. It was also necessary to classify the cure agents as either crystalline or glassy materials. It was reasoned that crystallinity might not be a necessity, but that it would probably be a factor in limiting the solubility of the solids in the binder. The emphasis of the program is placed on solid, blocked isocyanates for several reasons: (1) The synthesis are convenient from a variety of commercially available raw materials with two possible candidates (monoadducts and diadducts) from each phenol/diisocyanate pair, and (2) the unblocked low molecular weight diisocyanate should dissolve and diffuse into the binder phase more readily than a higher molecular weight conventional diisocyanate. The higher molecular weight is required to produce non-soluble compounds with melting points high enough to be of interest.

Task 2 was designed to investigate the solubilities of candidate, crystalline, solid blocked isocyanates with a range of melting points (chosen from the catalog prepared in Task 1) in typical plasticizers such as dioctyl adipate (DOA) and triacetin (TA), and in typical urethane forming polymers with a broad range of polarities such as hydroxyl terminated polybutadiene (HTPB) and polyethylene glycol (PEG). As noted earlier, it is necessary that the cure agents not be soluble in the binder medium; thus, on the basis of these results it was decided which blocked isocyanates to use in Task 3, the cure studies.

Infrared Spectroscopy (IR) was employed to further characterize and learn about the structure of the blocked isocyanates; for example, whether the compounds were the mono or di-blocked adducts of the diisocyanate. Infrared analysis was chosen as the primary means of analyzing the cure agents because of the distinct peaks in the IR spectrum of the isocyanate (NCO) and blocked isocyanate (NHCOO-) groups.

Task 3 was designed to demonstrate the validity of the hypothesis that gumstocks prepared with solid, blocked isocyanates in place of the free isocyanate do not cure at temperatures below the melting point of the cure agent, but cure rapidly when the temperature is raised above the melting point of the solid. To show the utility of this chemistry, cures were demonstrated in gumstocks prepared both with and without solid filler ingredients (such as

carbon), and using cure agents with a range of melting ("trigger") temperatures.

The effect of added urethane cure catalysts, such as dibutyltin dilaurate, on cure time and quality was also investigated.

Also, cure profiles were measured by changes in viscosity with time and temperature, and cure quality was determined by physical tests such as penetrometer measurements. These measurements were supplemented with IR analysis when more detail was desired.

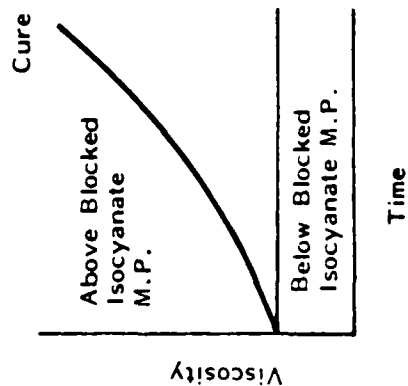
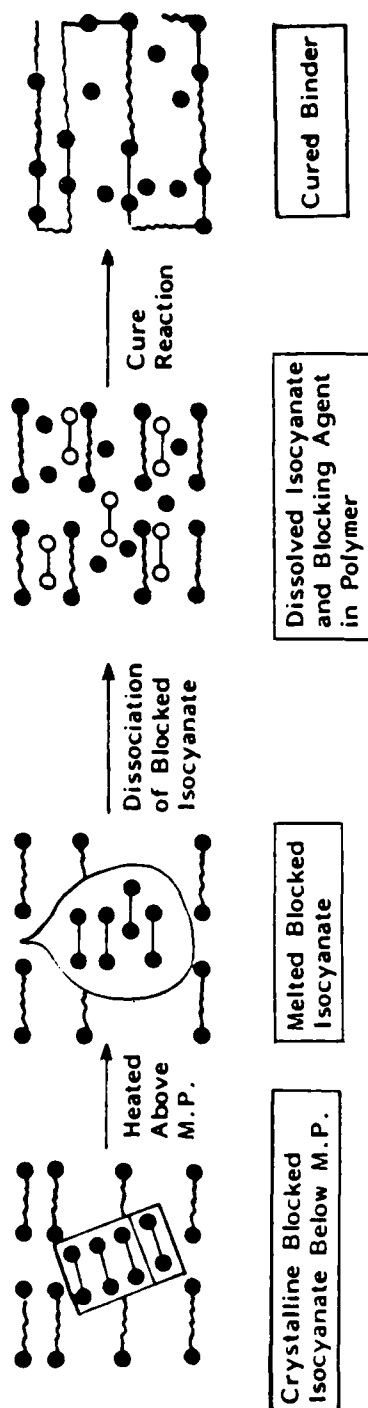
Particle size reduction techniques were also examined to determine the effect of particle size on cure quality. Gumstocks were prepared with unground blocked isocyanates that had been ground with a mortar and pestle, and with isocyanates that had been ground in a ball mill grinder for various lengths of time. The particle size of the blocked isocyanates was determined by the Mine Safety Apparatus (MSA) techniques. It was believed that the more finely divided blocked isocyanates would result in more homogeneous cures, since the free isocyanate would be able to traverse minimal distances in the binder. The effect of particle size on cure quality was determined by penetrometer measurements and infrared analysis. The approach and organization of the effort is summarized in Figure 1.0-2.

1.5 ORGANIZATION OF REPORT

This report is organized according to the logical flow of technical information from blocked isocyanate synthesis through cure studies and evaluation. A synopsis of Task 1 is presented in Section 3.0. In Section 4.0, a review of Task 2 is presented. Task 3 is summarized in Section 5.0. General conclusions and recommendations are reported in Section 6.0, and the key findings are listed in Section 7.0.

1.6 REFERENCES

1. United States and foreign patents obtained by William H. Graham and Inella G. Shepard include: Unites States, 4110135 and 4184031; France, 7733953; United Kingdom, 0046509; Israel, 0053183; Japan, 0129189; Sweden, 7712147; Canada, 290.643.
2. Contract DAAH01-75-C-0128; Report No. RK-CR-76-15, "High Rate Propellant Processing Technology".
3. U.S. Army Missile Command Contract No. DAAK40-76-C-1243.
4. Contract No. F04611-77-C-0028; Report No. AFRPL-TR-79-38, "Low Cost Binder Development" and Contract No. F04611-75-0059; Report No. AFRPL-TR-79-52, "Low Cost Motor Demonstration".
5. Contract F04611-80-C-0001, Report No. AFRPL-TI-82-087, "Solid Propellant Cure Catalyst Program, Final Report", 1980.
6. Unites States and foreign patents obtained by William Graham and Inella G. Shepard include: United States 4098626, 4165421, 4234738, and 4263444; Britain, 1560981; Israel, Pending.



- Synthesis of Blocked Isocyanates (●—●)
- From Phenol (●) and Diisocyanate (O—O)
- Compile Catalog of Blocked Isocyanate Melting Points (M.P.)
- Relationship of Molecular Structure, Melting Temperature, Binder Solubility, and Particle Size of Blocked Isocyanate
- Cure Profile in Hydroxyl Functional Polymers (●—●—●)
- Catalysis of Cure Reaction

Figure 1.0-2. Control of the Urethane Cure Reaction With Solid Blocked Isocyanates.

7. a) Contract No. DAAK40-78-C-0267; Report No. TR-RK-CR-80-7, "Low Cost Propellant Development Program".
b) Contract No. DAAH01-80-C-1093, "Non-NG Minimum Signature Propulsion System Evaluation".
c) R. T. Davis, J. D. Byrd, K. E. Bevel, and I. G. Shepard; "Application of Blocked Isocyanate Liner Technology to Minimum Smoke Liners"; 1981 JANNAF Propulsion Meeting.
8. Z. W. Wicks, Progress in Organic Coatings, 3, 73 (1975).
9. J. E. Leffler and W. H. Graham, J. Phys. Chem., 63, 687 (1959).

1.7 Personnel

The Principal Investigator for this program was Dr. William H. Graham, Group Supervisor, Propellant Research Group, Morton Thiokol, Inc./Huntsville Division. The Chemist for the program was Richard E. Boothe, also of Morton Thiokol, Inc./Huntsville Division. Early effort on the program in support of Dr. Graham was performed by Mrs. Inella G. Shepard. Mr. J. W. Blanks was responsible for performing all of the chemical analyses.

2.0 KEY FINDINGS AND ACCOMPLISHMENTS

The most significant results are listed below. The results are discussed in more detail in pertinent sections of the report, and are presented here under categories of blocked isocyanate synthesis and characterization, and cure studies.

- Blocked Isocyanate Synthesis and Characterization
 - Prepared a catalog of 25 solid, blocked isocyanates
 - Blocked isocyanates were characterized by x-ray crystallography, IR analysis, differential scanning calorimetry (DSC) and particle size analysis.
- Cure Studies
 - Demonstrated cures of blocked isocyanates with melting points varying from 60°C to 180°C in both carbon filled and non-carbon filled gumstocks. Cures were successful in gumstocks containing several different polyols and plasticizers.
 - Established that gumstocks held at 5°C below the melting point of the blocked isocyanate do not cure, but curing occurs quickly after raising the gumstock temperature above the melting point.
 - Compared cure rates in catalyzed and non-catalysed gumstocks; as expected, the catalyzed gumstocks (DBTDL, TPB) cured more quickly than the non-catalyzed.
 - Demonstrated rapid cures at 145°F in a common rocket motor liner formulation which did not cure at 130°F.
 - Examined solubilities of candidate blocked isocyanates in common polyalcohols and plasticizers.
 - Demonstrated cures in two standard composite propellant formulations at 145°F.

3.0 SYNOPSIS OF TASK 1

3.1 GENERAL

The first task in the overall approach of demonstrating that solid, blocked isocyanates can be used to control the cure profile of polyalcohol, isocyanate reactions was to synthesize a series of solid isocyanates with a range of melting ("trigger") temperatures.

This section reviews the synthesis of the blocked isocyanates, and is organized as follows: (1) synthesis of blocked isocyanates, (2) examination by x-ray scattering measurements, (3) melting point determination by differential scanning calorimetry.

3.2 SYNTHESIS OF BLOCKED ISOCYANATES

The solid, blocked isocyanates were prepared by reacting difunctional isocyanates with mono and dinitrophenols of various structure, salicylate esters, amides, and anilines. A list of the compounds used in these syntheses and their structures and name abbreviations is given in Table 3.0-1.

The synthesis of the blocked isocyanates was carried out in methylene chloride solution (CH_2Cl_2), with equimolar amounts of the diisocyanate and blocking agent. Triethylamine was used as the reaction catalyst. In most cases the blocked isocyanate, when formed, precipitated from the CH_2Cl_2 solution and was collected by filtration. In a few instances it was necessary to remove the CH_2Cl_2 by evaporation, and the solid cure agent was left behind. A more detailed account of the synthesis is given in Appendix A.

A catalog of 25 solid, blocked isocyanates was prepared; a list of the compounds, their melting points, and x-ray diffraction results (which determines crystallinity) is given in Table 3.0-2. It should be noted that the cure agents presented in Table 3.0-2 are all mono-blocked adducts of the diisocyanate, i.e., only one of the two isocyanate groups of the diisocyanate is reacted with the blocking agent. Thus, the catalog could be expanded by a factor of two by preparing the di-blocked adducts of the isocyanates. An example of several typical blocking reactions is shown in Figure 3.0-1.

3.3 X-RAY STUDIES

Examination of Table 3.0-2 shows that fewer than one-half of the solid, blocked isocyanates are crystalline materials; most are glasses. However, the crystalline blocked compounds have a range of melting points (from 60°C - $>275^\circ\text{C}$), which is a wide range of "trigger" temperatures from which to choose. It may be that the glasses will also perform satisfactorily in controlling cure profiles, but the crystalline blocked isocyanates were used in the cure studies (Task 3) since they tended to have more distinct, sharper melting points.

TABLE 3.0-1

A LIST OF COMPOUNDS AND THEIR STRUCTURES USED IN
THE SYNTHESIS OF SOLID, BLOCKED ISOCYANATES

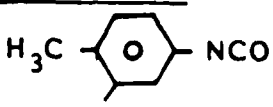
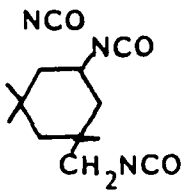

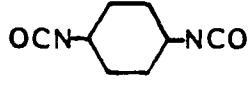
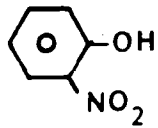
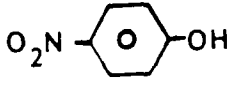
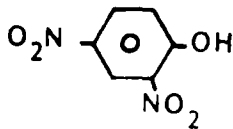
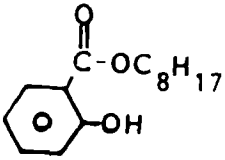
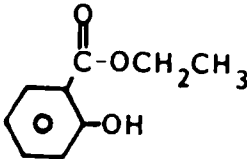
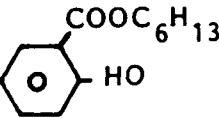
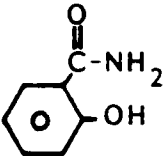
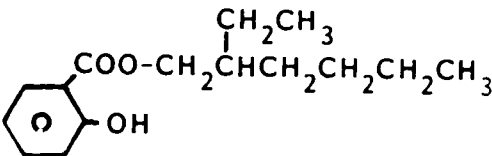
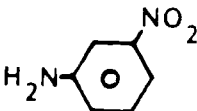
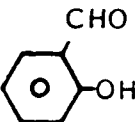
<u>COMPOUND</u>	<u>ABBREVIATION</u>	<u>STRUCTURE</u>
Toluene-2,4-diisocyanate	TDI	
Isophorone diisocyanate	IPDI	
para-Phenylene diisocyanate	Elate 160	
trans-1,4-Cyclohexane diisocyanate	Elate 166	
2-Nitrophenol	2-NP	
4-Nitrophenol	4-NP	
2,4-Dinitrophenol	2,4-DNP	
n-Octyl salicylate	OS	

Table 3.0-1 (Continued)

A List of Compounds and Their Structures Used in the
Synthesis of solid, Blocked Isocyanates

<u>COMPOUND</u>	<u>ABBREVIATION</u>	<u>STRUCTURE</u>
Ethyl salicylate	ES	
n-Hexyl salicylate	HS	
Salicylamide	SAM	
α-Ethyl-hexylsalicylate	EHS	
meta-Nitroaniline	MNA	
Salicylaldehyde	SA	

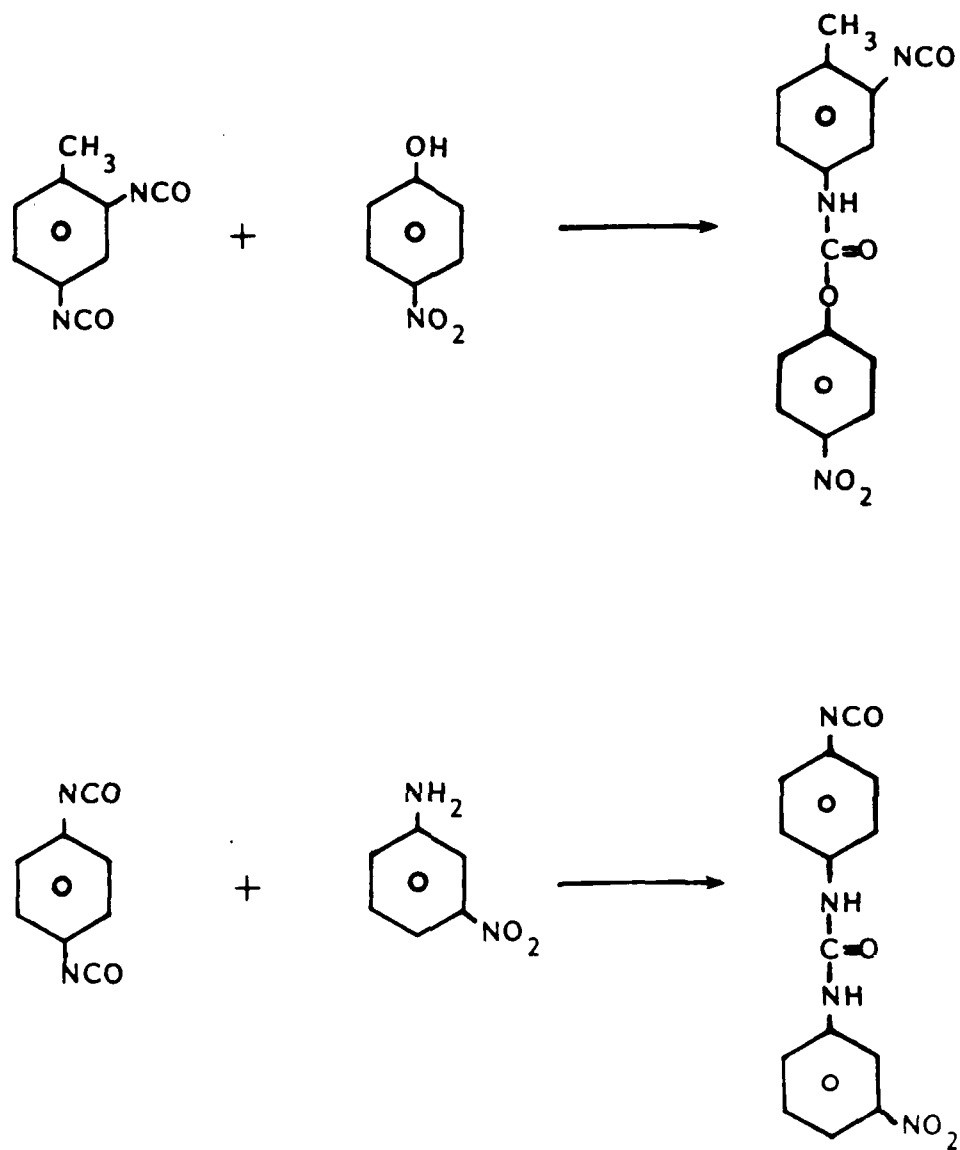


Figure 3.0-1. Several Typical Blocking Reactions.

TABLE 3.0-2

LIST OF PREPARED SOLID, BLOCKED ISOCYANATES

<u>Blocked Isocyanate</u>	<u>DSC Melting Point (°C)</u>	<u>Crystalline/Glass</u>
TDI/2-NP	150 (2 peaks)	Crystalline
TDI/4-NP	180 (2 peaks)	Crystalline
TDI/2,4-DNP	65	Crystalline
IPDI/2-NP	60-80 (2 peaks)	Glass
IPDI/4-NP	60-70	Glass
Elate 166/2,4-DNP	>205	Crystalline
Elate 166/2-NP	>275 (broad endotherm)	Crystalline
Elate 166/4-NP	250	Crystalline
Elate 160/2,4-DNP	128	Crystalline
Elate 160/2-NP	180-185	Glass
Elate 160/4-NP	245 (2 peaks)	Crystalline
TDI/OS	100-108	Glass
TDI/ES	85-88	Glass
TDI/HS	65-75	Glass
TDI/SAM	131-135	Glass
TDI/EHS	185-190	Glass
TDI/MNA	75-80	Crystalline
IPDI/MNA	130	Crystalline
IPDI/SAM	108-112	Glass
Elate 160/MNA	>230	Glass
Elate 166/SAM	>275	Glass
Elate 160/SAM	>265	Glass
TDI/SA	>160	Glass
IPDI/ES	115-120	Glass
IPDI/SA	80-85	Glass
Elate 160 *	97-101	Crystalline
Elate 166 *	64-66	Crystalline

* Commercial diisocyanates (Armak)

3.4 DSC ANALYSIS

The basic function of a differential scanning calorimeter (DSC) is to measure the amount of heat required to raise the temperature of a sample at a predetermined rate. When a sample is analyzed by DSC, a positive or negative peak is seen when the sample begins to absorb (endotherm) or emit (exotherm) heat. This peak corresponds to the temperature at which the sample begins to melt, decompose or react. Thus, from a DSC trace, one can determine the melting point of a compound. In the case of a blocked isocyanate, the temperature at which the sample begins to absorb heat is the unblocking temperature; this temperature is that at which the blocked isocyanate group becomes unblocked and is therefore free to react with a polyol. Several examples of DSC traces are shown in Figure 3.0-2, and more can be found in Appendix B. The DSC trace of several of the cure agents showed more than one peak, or more than one temperature at which the compound absorbed heat. This is probably due to both unblocking and decomposition, but could also be due to volatilization; the melting point in these instances is taken to be the lower temperature of the two heat absorptions.

4.0 SYNOPSIS OF TASK 2

4.1 GENERAL

The second task in the overall project approach was to examine the prepared solid blocked isocyanates by conventional methods, such as IR, and learn something about the solubilities of these compounds in typical urethane forming polymers(such as HTPB and PEG) and plasticizers (such as DOA and triacetin).

This section reviews the analysis of the cure agents by IR and the solubility studies, and is organized as follows: (1) IR analysis, (2) solubility studies.

4.2 INFRARED ANALYSIS

Infrared spectroscopy (IR) is a convenient method of analyzing solid, blocked isocyanates. Both the unblocked isocyanate (NCO) peak and the blocked (NHCOOR) peak occur at distinctive wavelengths in the spectrum; therefore, it is easily determined whether one or both of these two functionalities is present in a molecule. An example of this is shown in Figure 4.0-1. The mono-blocked isocyanate shown in Figure 4.0-1 is TDI/2-NP; the NCO peak is seen at 2300 cm^{-1} , and the NHCOO peak is at 1700 cm^{-1} . The amide II peak can be seen at 1525 cm^{-1} .

Because of the wide separation and distinct wavelengths of the NCO and NHCOO functionalities, IR is also a convenient method of following blocking and unblocking reactions of the isocyanate groups. An example of such a reaction is shown in Figure 4.0-2. In this figure is shown the unblocking of TDI/2-NP as followed by IR. Initially, both NCO and NHCOO peaks are seen; as the compound

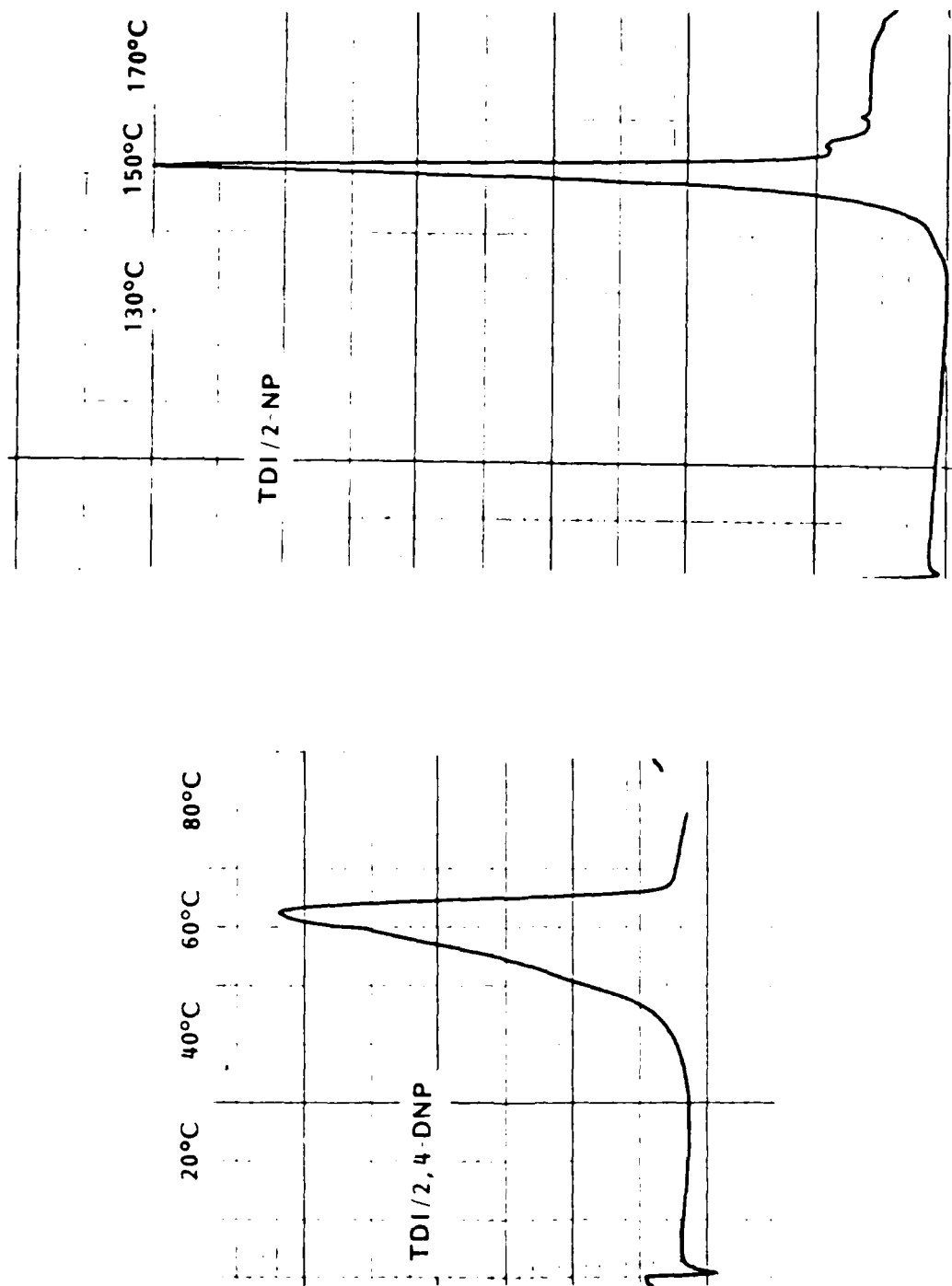


Figure 3.0 2. Examples of Typical DSC Plots.

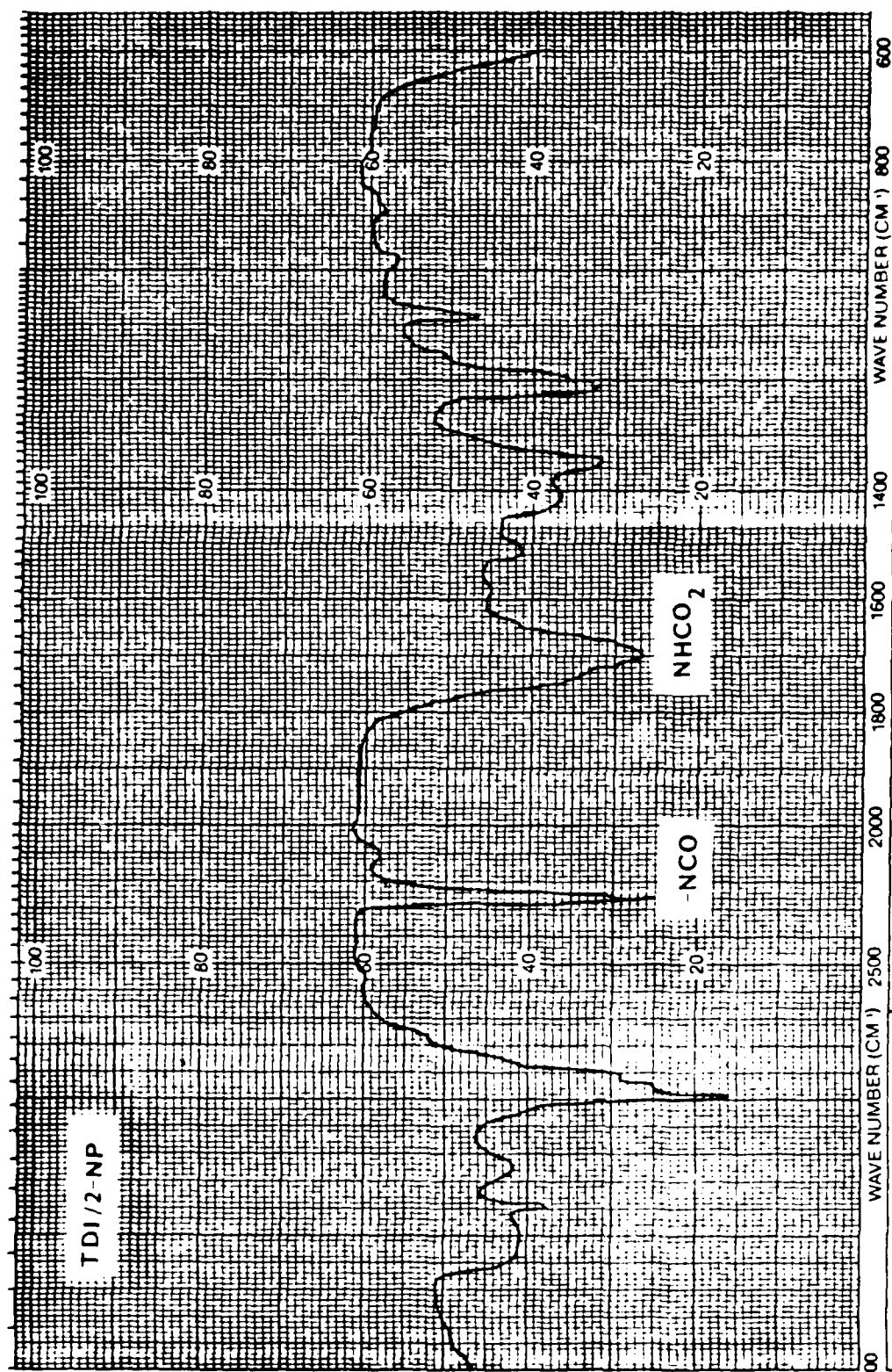


Figure 4.0 1. IR Spectrum Showing NCO and NHCO₂ Peaks.

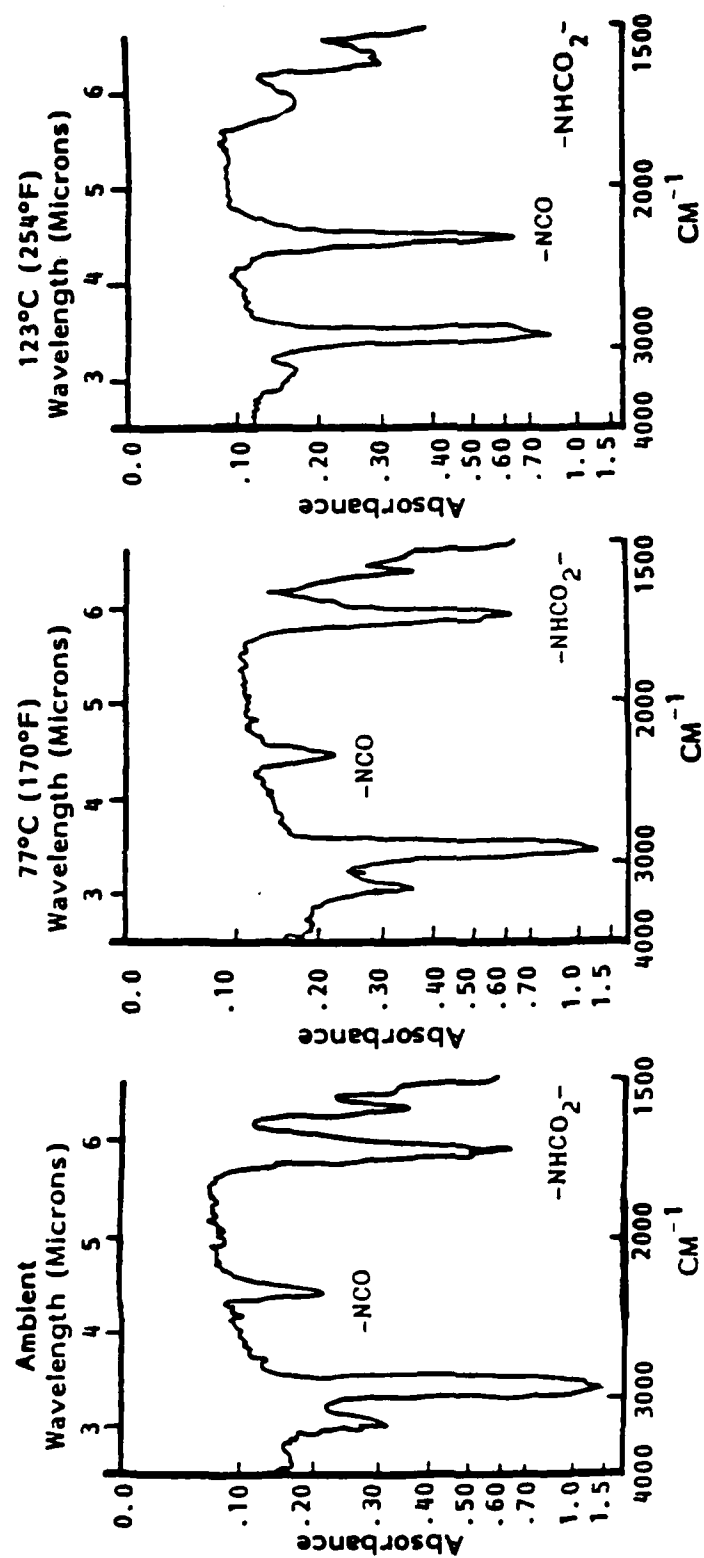


Figure 4.0-2. Unblocking of Mono-blocked TDI/2-NP.

unblocks, the NCO peak increases in intensity, and the NHCOO peak concurrently decreases in intensity.

The cure agents listed in Table 3.0-2 were analyzed by IR; their spectra are given in Appendix C. In each of the spectra is seen both the NCO and NHCO_2 peaks, indicating that the compounds are the mono-blocked adducts.

It was observed that, periodically, the melting point of the blocked isocyanates varied slightly from batch to batch. Though the diisocyanate and blocking agent were reacted in a 1 to 1 molar ratio so that the mono-blocked adduct would be obtained, undoubtedly a small proportion of the diisocyanate doubly blocks, causing the melting point to vary slightly. The melting point difference from batch to batch was small, typically 1°C to 2°C . One can see, however, from the spectra, that the products of the diisocyanate and blocking agent were predominately the mono-blocked adduct.

It was noted that the intensity of the isocyanate peak often decreased upon storage of the blocked isocyanates. The reason for this loss has not been determined, but may be due to a post-reaction dimerization or polymerization of the unblocked isocyanate group or to reaction with the NH of the carbamate linkage of the phenol reaction product.

4.3 SOLUBILITY STUDIES

As noted earlier, the key property of the solid, blocked isocyanates is that they be insoluble in the binder phase prior to dissociation. Usually, the reactivity of most molecules is greatly inhibited in the crystalline state. If the blocked isocyanate were soluble, it would be reactive. More generally, the whole concept of crystal lattice stabilization of the blocked isocyanate above its melting point would be inoperable upon dissolution of the solid phase.

In order to investigate the solubilities of blocked isocyanates, several crystalline and glassy cure agents were mixed with common urethane forming polymers and plasticizers. The results of these experiments are shown in Table 4.0-1.

The solubilities of the cure agents were examined in each of the polyols and plasticizers at both ambient (room) temperature and at 5°C below their melting points and were determined by comparison of the weight of undissolved blocked isocyanate to the total amount of cure agent mixed with the polyol and plasticizer. Of the cure agents examined, only IPDI/2-NP and IPDI/4-NP were soluble; they were soluble in every polyol and plasticizer examined, both at room temperature and at 5°C below their melting points. The solubility of both cure agents at room temperature was approximately 0.5 g/ml, and when the temperature was raised became completely soluble. The other cure agents were not at all soluble at room temperature or at 5°C below their melting point.

The x-ray scattering measurements showed both IPDI/2-NP and IPDI/4-NP to be glasses, and the other blocked isocyanates examined in the solubility studies to be crystalline (Table 3.0-2). Only

TABLE 4.0-1

SOLUBILITY STUDIES

	R45M/AO Ambient	5°C<	PEG 4000 Ambient	5°C<	DOA Ambient	5°C<	Triacetin Ambient	5°C<
TDI/2,4-DNP	insol.	insol.	insol.	insol.	insol.	insol.	insol.	insol.
IPDI/2-NP	.5 g/ml	soluble	.4 g/ml	soluble	.5 g/ml	soluble	.5 g/ml	soluble
TDI/4-NP	insol.	insol.	insol.	insol.	insol.	insol.	insol.	insol.
Elate 160/2-NP	insol.	insol.	insol.	insol.	insol.	insol.	insol.	insol.
Elate 160/2,4-DNP	insol.	insol.	insol.	insol.	insol.	insol.	insol.	insol.
IPDI/4-NP	.6 g/ml	soluble	.6 g/ml	soluble	.5 g/ml	soluble	.5 g/ml	soluble

IPDI/2-NP and IPDI/4-NP were soluble in the polyols and plasticizers examined, thus, as expected, it seems that the glassy materials are unsuitable cure agents due to the possibility of dissolution into the binder.

5.0 SYNOPSIS OF TASK 3

5.1 GENERAL

The third task in the program approach was to perform cure studies with blocked isocyanates of various melting points (chosen on the basis of crystallinity and insolubility in the binder materials), and to investigate the effect of particle size, catalysts and temperature on cure time and quality.

This section summarizes the results of Task 3, and is organized as follows: (1) cure studies, (2) effect of added cure catalysts, (3) effect of particle size on cure quality, (4) liner formulations, (5) propellant formulations.

5.2 CURE STUDIES

5.2.1 Non-Carbon Filled Gumstocks

The viability of solid, blocked isocyanates to control the urethane cure reaction was first demonstrated in non-carbon filled gumstocks. Table 5.0-1 lists the cure agents used in preparing the gumstocks, and a detailed account of the gumstock ingredients is given in Appendix D. The gumstocks were kept at 5°C below the melting point of the cure agent for two days and no curing occurred, but rapid (<1 day) cures were observed when the mixtures were heated at 5°C above the "trigger" temperature. Cures were demonstrated in gumstocks containing several different urethane forming polymers (HTPB, PEG 4500) and plasticizers -- dioctyl adipate (DOA), triacetin, and over a temperature range of 65-180°C; no tensile data were collected, but good, hard, rubbery cures were obtained. The weight percentage of ingredients which produced the best cures was 7-8% blocked isocyanate, 53-57% polyol, and 33-36% plasticizer.

5.2.2 Carbon Filled Gumstocks

Control of the urethane cure reaction with solid, blocked isocyanates was also demonstrated in carbon filled gumstocks. The cure agents used in preparing the gumstocks are listed in Table 5.0-2, and a detailed account of the polyol, plasticizer, carbon and blocked isocyanate content of each mix is given in Appendix E. Again, gumstocks kept at 5°C below the melting point of the cure agent showed no evidence of curing after two days, but rapid cures occurred within 1 day when the temperature was raised above the "trigger" temperature. The weight percentage of components which produced the best cures was 11-12% blocked isocyanate, 32-36% polyol, 43-48% plasticizer and 4-5% carbon.

TABLE 5.0-1
BLOCKED ISOCYANATES USED IN PREPARING
NON-CARBON FILLED GUMSTOCKS

<u>Cure Agent</u>	<u>Trigger Temperature (°C)</u>
Elate 160/2-NP	180
TDI/4-NP	175
Elate 166/2,4-DNP	155
TDI/2-NP	130
Elate 160/2,4-DNP	128
TDI/2,4-DNP	65

TABLE 5.0-2
BLOCKED ISOCYANATES USED IN PREPARING
CARBON FILLED GUMSTOCKS

<u>Blocked Isocyanate</u>	<u>Trigger Temperature (°C)</u>
Elate 160/2-NP	180
TDI/4-NP	175
TDI/2-NP	130
Elate 160/2,4-DNP	128
TDI/2,4-DNP	65

5.2.3 Cure Profiles

The cure profiles of the carbon-filled gumstocks listed in Table 5.0-2 were measured by following the changes in viscosity with time and temperature, and by penetrometer measurements on the cured material. The results of these experiments are shown in Table 5.0-3. The initial viscosity of the gumstocks was quite low (<1 kp), and when heated to within 5°C of the cure agent melting point the viscosity increased, but only slightly. After two days at 5°C below the blocked isocyanate melting point no further increase in viscosity was observed. The gumstocks cured to different degrees of hardness, but all were good, rubbery cures.

5.2.4 Gumstocks With Mixtures of Blocked and Unblocked Isocyanates

The viscosity of the carbon filled and non-carbon filled gumstocks increased slightly when the temperature of the mixtures was raised from ambient to within 5°C of the cure agent melting point. The initial viscosity of the gumstocks was low, and the viscosity near the "trigger" temperature, though a bit higher, was still quite low. It was expected that the cure profile could be changed by using mixtures of blocked isocyanate and free diisocyanate in the gumstocks; the blocked isocyanate is unreactive, but the free diisocyanate can react with the polyol, resulting in partial curing and therefore higher viscosity.

A series of gumstocks was prepared with constant amounts of R45M/AO (AO (antioxidant) 2246 was used), DOA and carbon, but with various relative amounts of liquid TDI and TDI blocked with 2-nitrophenol. The viscosity of the gumstocks was measured at room temperature, then the mixes were heated to within 5°C of the melting point of TDI/2-NP and, the viscosity was remeasured. The results of these experiments are given in Table 5.0-4. As with the gumstocks containing solely blocked isocyanate, the initial viscosity of these mixtures was low, from 0.01 to 0.02 kilopoise. There was surprisingly little difference in initial viscosity between the gumstocks containing 95% TDI/2-NP and 25% TDI/2-NP. However, the viscosity of the mixes at 5°C below the melting point of TDI/2-NP was quite different. The viscosity of the gumstocks containing 95, 90 and 80 percent TDI/2-NP increased only slightly; the profile of these mixes was similar to that of the gumstocks containing only blocked isocyanate (Table 5.0-3). The viscosity of the gumstocks with 70 and 60 percent TDI/2-NP increased more dramatically, to 8 and 50 kp, respectively. The gumstocks containing less than 60 percent TDI/2-NP cured to a rubbery state, and viscosity measurements could not be obtained. All of the gumstocks, when placed at 5°C above the melting point of TDI/2-NP, cured well (as the penetrometer measurements indicate), and it is interesting to note that the gumstock which cured the hardest was the one containing the highest relative ratio of TDI/2-NP to liquid TDI.

As expected, the profile of the cure reactions changed considerably when mixtures of blocked isocyanate and free diisocyanate were employed. By changing the relative amount of blocked isocyanate to free diisocyanate some degree of control over the cure profile was

TABLE 5.0-3
CURE PROFILES OF CARBON FILLED GUMSTOCKS

<u>Cure Agent</u>	<u>Viscosity at Ambient</u>	<u>Viscosity at 5°C Below Melting Point</u>	<u>Penetrometer Measurement on Cured Gumstock</u>
Elate 160/2-NP	<1 kp	1 kp	37
TDI/4-NP	<1 kp	2 kp	32
TDI/2-NP	<1 kp	1 kp	80
Elate 160/2,4-DNP	<1 kp	3 kp	90
TDI/2,4-DNP	<1 kp	<1 kp	60

TABLE 5.0-4
CURE PROFILES OF GUMSTOCKS PREPARED WITH
TDI LIQUID AND TDI/2-NP

<u>Relative % TDI/2-NP to TDI Liquid</u>	<u>Viscosity at Ambient</u>	<u>Viscosity at 5°C Below TDI/2-NP Melting Point</u>	<u>Penetrometer Measurement of Cured Material</u>
95:5	.02 kp	.04 kp	13
90:10	.01 kp	.02 kp	35
80:20	.01 kp	.018 kp	23
70:30	.01 kp	8 kp	17
60:40	.02 kp	50 kp	19
50:50	.01 kp	Rubbery Cure	25
25:75	.01 kp	Rubbery Cure	27

obtained; it is expected that proper manipulation of the blocked isocyanate/liquid diisocyanate ratio would enable partial cure of a mixture to a desired viscosity at one temperature, and complete cure at another temperature. This may have application in processes where it is necessary to partially cure a material, cast or mold it, and then have it completely cure.

5.3 EFFECT OF ADDED CURE CATALYSTS

To examine the effect of catalysts on the curing of mixtures containing blocked isocyanates and polyols, two gumstocks containing TDI/2,4-DNP and R45M/AO were prepared. To one of the gumstocks was added 2 drops of dibutyltin dilaurate (DBTDL), a quick cure catalyst; no catalyst was added to the other gumstock. An IR spectrum of the mixtures at ambient temperature is shown in Figure 5.0-1. The NCO peak (resulting from the unblocked isocyanate group of TDI/2,4-DNP) is seen at 2300 cm^{-1} , and the NHCO_2 (resulting from the blocked isocyanate functionality) peak (small) is seen at 1720 cm^{-1} . After two days of ambient temperature the samples were again analyzed by IR, which showed that no curing of the samples had occurred. The same was true after 2 days at 5°C below the melting point of TDI/2,4-DNP; still no curing was observed. The gumstocks were then heated to 5°C above the melting point of TDI/2,4-DNP or 70°C , and the samples were periodically analyzed by IR spectroscopy. Within 2 hours of raising the temperature over the cure agent melting point, the gumstock to which DBTDL was added appeared to be nearly cured. An IR of this mixture is shown in Figure 5.0-2; the NCO peak has almost completely disappeared and the NHCO_2 peak has dramatically increased in intensity. This indicates that curing has taken place to a large degree. An IR of the sample to which no catalyst was added is shown in Figure 5.0-3; the fairly intense NCO peak indicates that the gumstock is still quite uncured. Both samples were returned to the 70°C temperature and both completely cured, but the catalyzed sample cured in three hours, whereas the uncatalyzed gumstock needed 2-3 days to completely cure. Thus, the DBTDL catalyst greatly decreased the cure time.

5.4 EFFECT OF BLOCKED ISOCYANATE PARTICLE SIZE ON CURE QUALITY

The blocked isocyanate particle size was expected to have a pronounced effect on cure quality. Finely divided particles should result in more homogeneous cures, because the free diisocyanate will be able to traverse minimal distances in the binder. The Mine Safety Apparatus Techniques were employed to measure the particle size of several cure agents. The results of the measurements are shown in Table 5.0-5.

Gumstocks prepared with blocked isocyanates of various particle sizes were heated at 5°C above the cure agent melting point for two days, then the cured samples were examined by penetrometer measurements; the results are presented in Table 5.0-6. As predicted, the gumstocks prepared with the more finely divided blocked isocyanates cured harder and were more homogeneous than the gumstocks containing the larger particles. If the cure agents were not ground

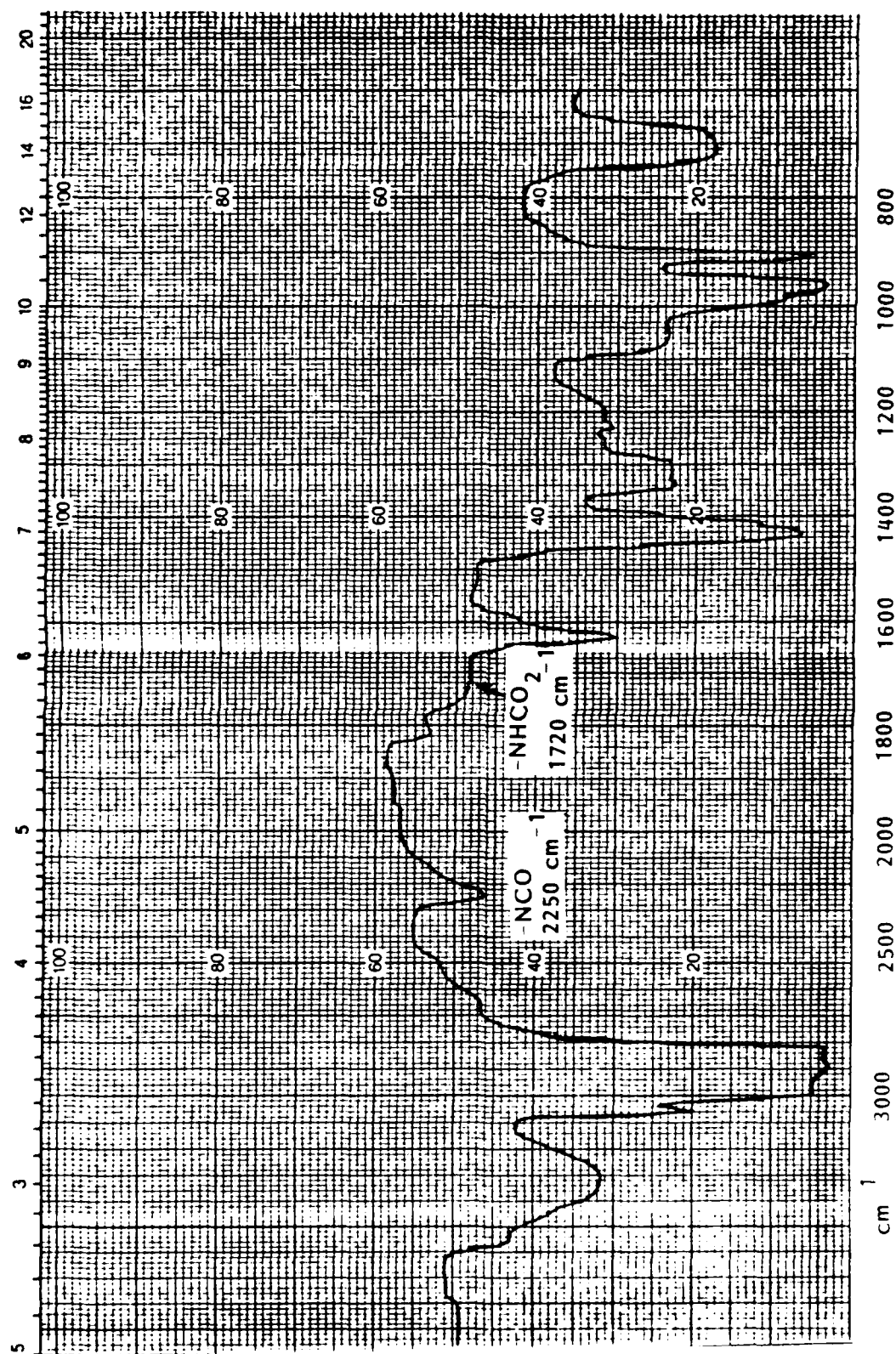


Figure 5.0-1. IR Spectrum of R45M/AO and TDI/2,4-DNP at Room Temperature.

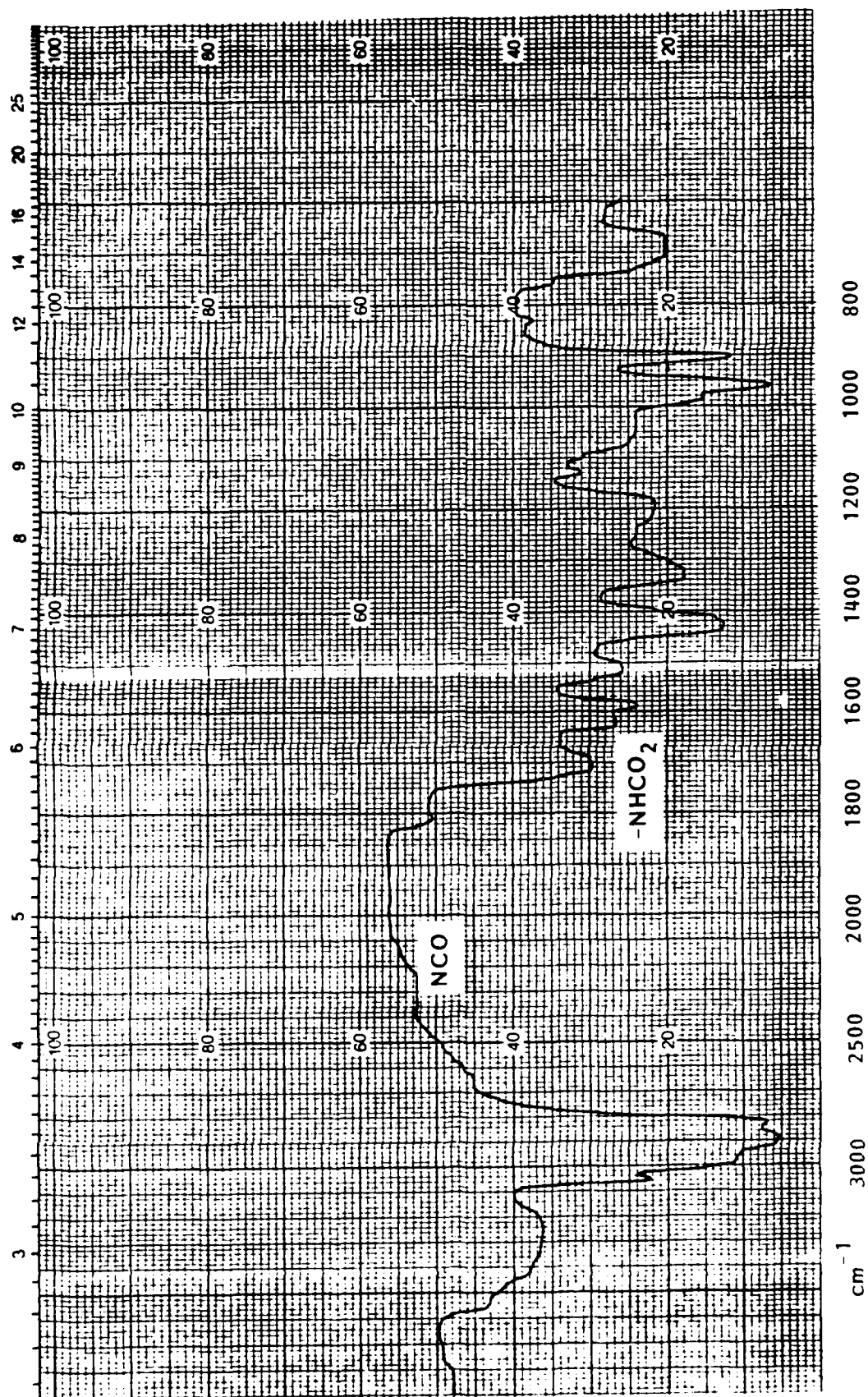


Figure 5.0-2. TDI/2,4-DNP and R45M/AO, DBTL Added, 2 Hours at 65°C.

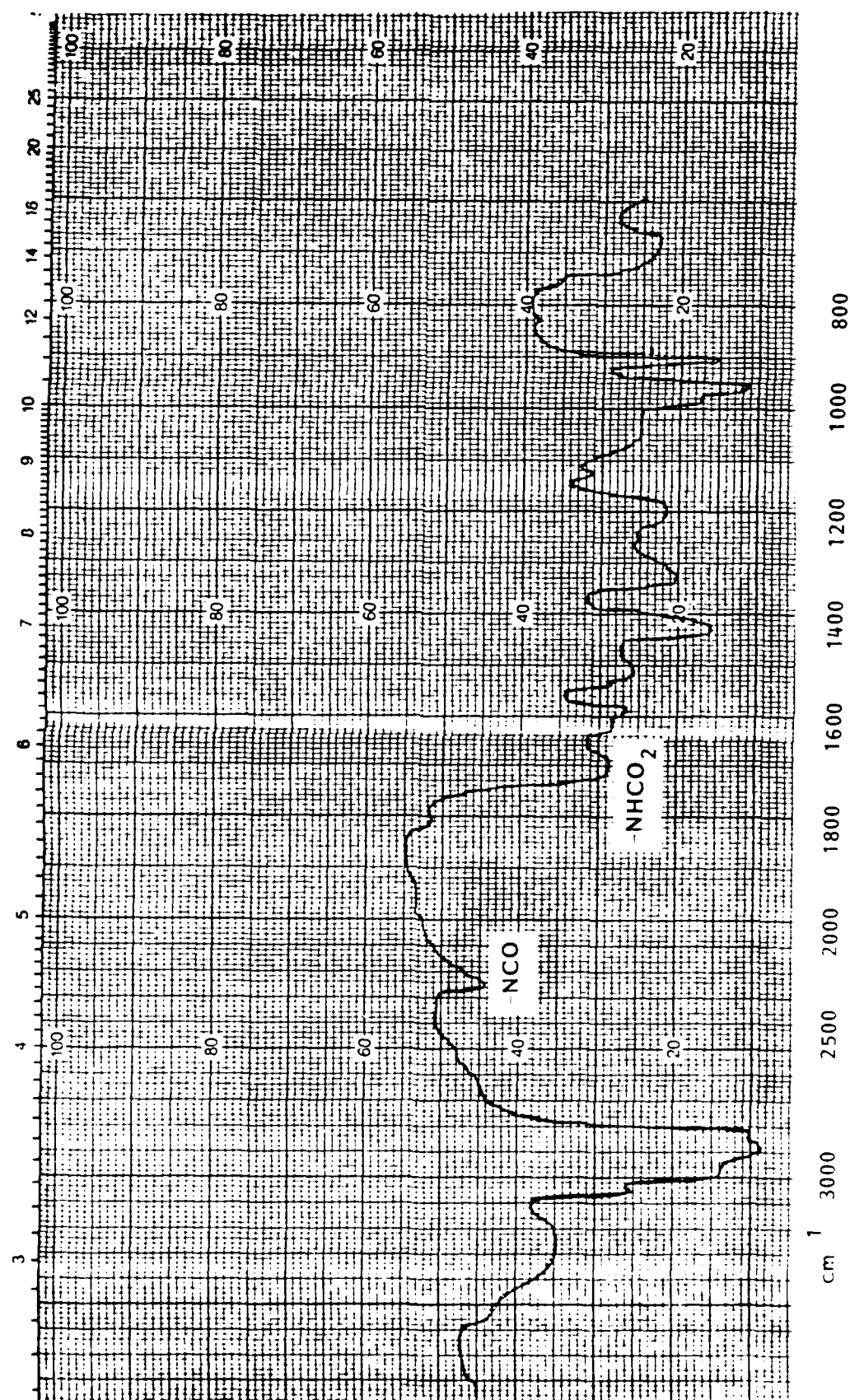


Figure 5.0 3. TDI/2,4-DNP and R45M/AO, No DBTDL, 2 Hours at 65°C.

TABLE 5.0-5
RESULTS OF PARTICLE SIZE MEASUREMENTS

<u>Blocked Isocyanate</u>	<u>Grinding Method and Time</u>	<u>Particle Size (microns)</u>
Elate 160/2-NP	Hand Ground With Mortar and Pestle	72
Elate 166/4-NP	Hand Ground With Mortar and Pestle	16
Elate 160/4-NP	Hand Ground With Mortar and Pestle	4
TDI/2,4-DNP	Hand Ground With Mortar and Pestle	50
TDI/2,4-DNP	Ground for 4 Hours In Ball Mill Grinder	4
TDI/2,4-DNP	Ground for 24 Hours in Ball Mill Grinder	2

TABLE 5.0-6
RESULTS OF CURES WITH BLOCKED ISOCYANATES
OF VARIOUS PARTICLE SIZES

<u>Blocked Isocyanate</u>	<u>Particle Size (microns)</u>	<u>Penetrometer Reading (ten seconds)</u>
TDI/2-NP ^a	85	Spotty, lumpy
TDI/2-NP ^b	40	70-75
Elate 160/2-NP ^a	110	Spotty, lumpy
Elate 160/2-NP ^b	72	30-40
TDI/2,4-DNP ^a	120	Did not cure
TDI/2,4-DNP ^b	50	85-95
TDI/2,4-DNP ^c	2	70

Notes:

- a) Collected from synthesis
- b) Hand ground with mortar and pestle
- c) Ground in ball mill grinder for 24 hours

at all before use (i.e., used directly after collection from synthesis), the cures were very "spotty", containing both cured and uncured sections. A significant improvement in cure quality was observed when the blocked isocyanates were ground with a mortar and pestle before use, but the cure hardness still varied slightly from section to section of the sample. The hardest, most homogeneous cures were obtained when the blocked isocyanate was ground in a ball mill grinder before use. The gumstock prepared with TDI/2,4-DNP which had been ground with a mortar and pestle cured well (the penetrometer reading varied from 85-95 through the sample), but the gumstock containing TDI/2,4-DNP which had been ground in the ball mill grinder was more homogeneous (the penetrometer reading was 70 throughout the sample) and a bit harder.

5.5 LINER FORMULATIONS

To demonstrate the potential of blocked isocyanates in liner applications, gumstocks of a common three component liner formulation were prepared with blocked isocyanates in place of the unblocked diisocyanate which is normally employed. However, gumstocks prepared at the weight percentage of materials normally used in the liner (46.3% R45M, 13.7% isocyanate and 40% carbon) were too viscous to be easily handled; changing from the free, liquid diisocyanate to the solid, blocked isocyanate increased the overall solids content mixture from 40% to 53%, and the result was a dramatic increase in viscosity. Thus, it was necessary to reduce the percentage of solids in the formulation to make the mixes less viscous. The formulation which produced the best cures, and had the most acceptable initial viscosity (approximately 1 kp), was 83% R45M/AO, 14% blocked isocyanate and 3% carbon. Though this was a drastic reduction in the percentage of carbon in the mix, the gumstocks prepared with this concentration of ingredients cured very well. The hardness and cure quality of the mixtures prepared with the blocked isocyanates was comparable to that of gumstocks prepared with free isocyanate at the normal liner concentration.

No curing of the liner gumstocks was observed over a two day period at temperatures of 5°C below the melting point of the blocked isocyanate, and good, rapid (<1 day) cures were obtained after raising the temperature to 5°C above the cure agent melting point.

The cure agents employed in the liner mix experiments and the results of the penetrometer measurements on the cured gumstocks are presented in Table 5.0-7.

5.6 PROPELLANT FORMULATIONS

To demonstrate the potential of blocked isocyanates in propellant applications, a high solids (88.25% AP) HTPB formulation was prepared with TDI/2,4-DNP as the cure agent. The high solids formulation was selected for this evaluation as it was being developed for a current application, and TDI/2,4-DNP was chosen as the cure agent because its melting point (65°C) is the temperature at which propellant mixes are commonly cured.

TABLE 5.0-7
RESULTS OF LINER FORMULATIONS

<u>BLOCKED ISOCYANATE</u>	<u>PENETROMETER READING OF CURED LINER GUMSTOCK (10 Seconds)</u>
TDI/4-NP	24
Elate 160/2,4-DNP	11
TDI/2-NP	10
Elate 160/2-NP	7

The end-of-mix (EOM) viscosity was high at 102 kp which made processing of the mix difficult. However, the high viscosity was not entirely due to the blocked isocyanate; the viscosity of the mix was high even before the cure agent was added. The blocked isocyanate may also have caused some dewetting, but it is difficult to separate the solids viscosity and dewetting effects. A sample of the mix heated for 4 days at 130°F (below the melting point of TDI/2,4-DNP) got harder, but did not cure. An attenuated total reflectance (ATR) IR spectrum of the sample is shown in Figure 5.0-4, the peak at 2300 cm^{-1} indicates unreacted NCO groups. A sample of the mix heated for 4 days at 145°F (above the melting point of TDI/2,4-DNP) cured very hard, but the tensile properties were a bit lower than desired; ambient stress was 96 psi, and strain was 9.5%. The burn rate of the sample at 1000 psi was 0.96 inches/second with a 0.65 exponent, both of which are comparable to the baseline propellant.

Because of the problems with viscosity in the 88.25% solids formulation, another mix with lower solids was prepared. The second mix contained 84% total solids, and a lower NCO/OH ratio than the first mix. Initially, the cure profile of this formulation was much better; the mix viscosity before addition of the cure agent was 1-2 kp, and the EOM viscosity was 16 kp at 110°F. However, potlife samples were tested at 77, 130 and 145°F, and, although the 130°F sample cured more slowly, both the 130°F and 145°F samples cured within 24 hours. The ambient sample, while curing still more slowly than the 130°F sample, had a viscosity of 400 Kp after 4 days. The reason for the premature partial curing of the 77°F and 130°F samples is not clear, but may be due to reaction between the aziridine bonding agent used in the mix and the polymer hydroxyl groups.

6.0 CONCLUSIONS AND RECOMMENDATIONS

- The viability of solid, blocked isocyanates to control the profile of the isocyanate/hydroxyl cure reaction has been demonstrated. The successful demonstration of the concept implies that other solid state compounds can be used to trigger desired reactions only above their melting point, providing temperature sensitive on-off control of chemical reactions.
- The crystalline solid, blocked isocyanates are insoluble in the binder materials at temperatures below their melting point. When the temperature is raised above the blocked isocyanates melting point during the cure phase, the material melts and/or dissociates to the reactive, soluble form and triggers the cure reaction. The glassy solid, blocked isocyanates are unsuitable cure agents because of their solubility in the binder materials at temperatures below their melting point.
- The potential for use of blocked isocyanates in liner and propellant applications needs to be investigated further. The reason(s) for the premature curing of propellant formulations containing TDI/2,4-DNP needs to be determined.

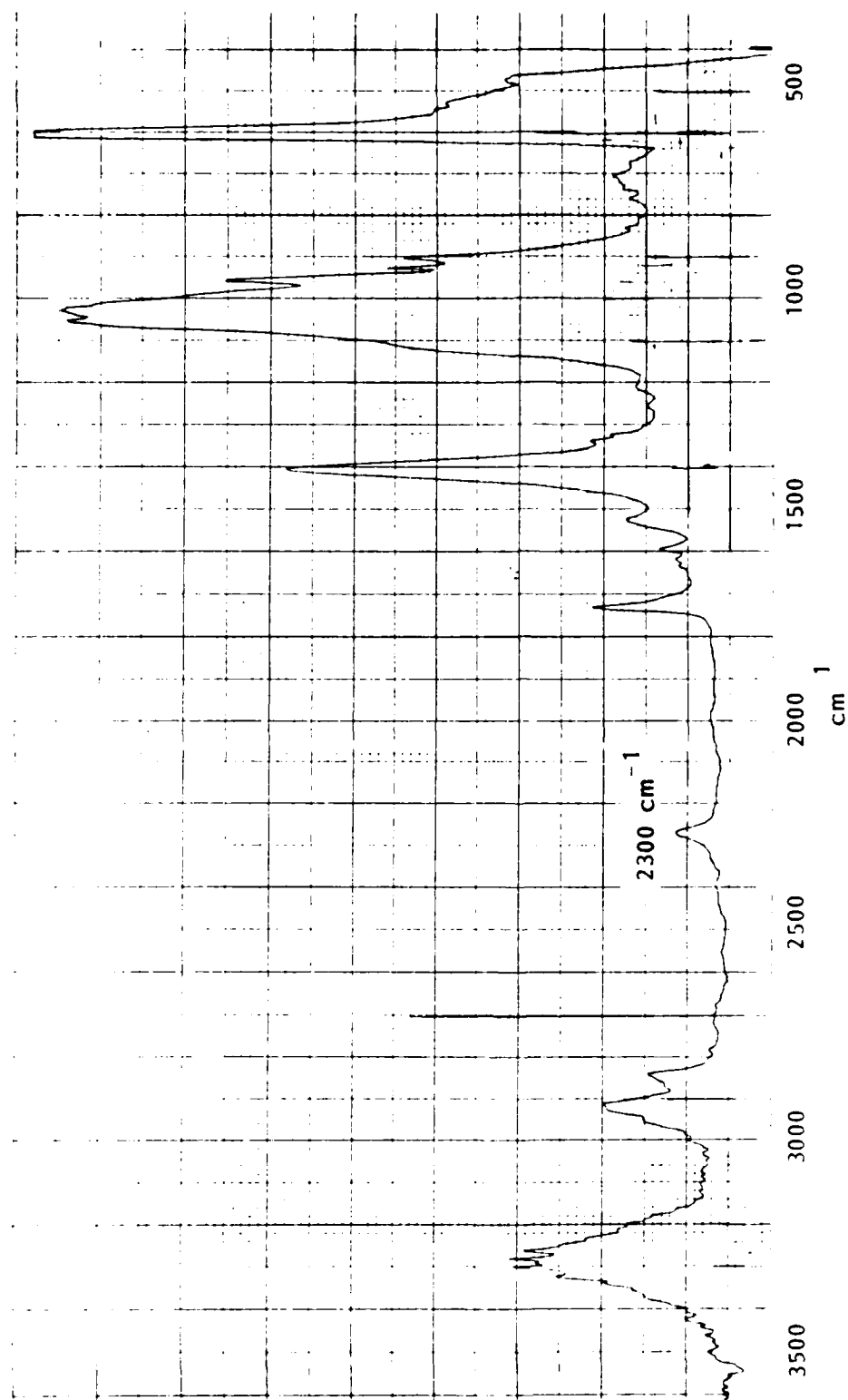


Figure 5.0 4. ATR Infrared Spectrum of Uncured Propellant.

- The profile of the hydroxyl/isocyanate cure reaction can be altered by using mixtures of blocked and unblocked isocyanates. This may prove to be useful in applications where it is necessary to partially cure material at one temperature, then completely cure later at a higher temperature.
- There is a direct correlation between the trigger temperature of the cure reaction and the melting point of the blocked isocyanate. Gumstocks held at 5°C below the melting point of the blocked isocyanate do not cure, and rapid curing occurs when the temperature is raised above the melting point.
- Infrared spectroscopy is a convenient technique for examination of isocyanates and blocked isocyanates because of the strong and isolated NCO and NHCO_2 absorptions.
- A major disadvantage that has become evident in utilizing the crystalline blocked isocyanates in filled systems is the inherent increase in viscosity in adding the solid, finely divided cure agent. To achieve the same level of active cure agent, the net result is the addition of 50% "inert" material in the form of the blocking agent.

APPENDIX A

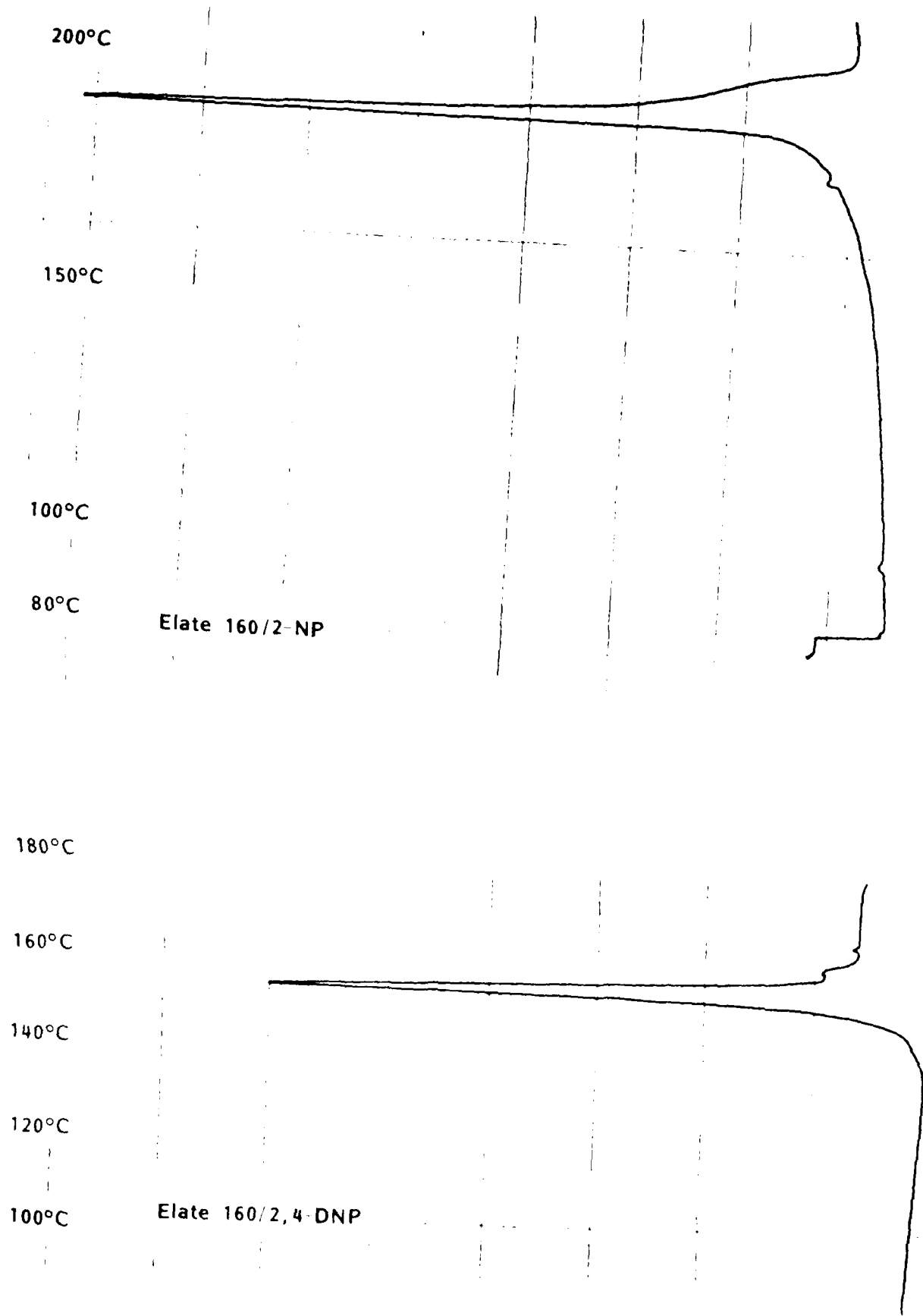
SYNTHESIS OF BLOCKED ISOCYANATES

For each batch of mono-blocked isocyanate prepared, twenty grams of the blocking agent were dissolved in 100 ml of methylene chloride (CH_2Cl_2). This solution was cooled to 0°C in ice water, and to the mixture was added an equimolar amount of the diisocyanate. The solution was mechanically stirred until a homogeneous mixture was obtained, then 2-3 drops of triethylamine were added as catalyst. The solution was mixed at 0°C until the blocked isocyanate precipitated (normally about 30 minutes to 1-1/2 hours), or until IR analysis showed that the diisocyanate had become blocked. If precipitation occurred, the solid was filtered from the solution and washed several times with CH_2Cl_2 . If no precipitate formed after IR showed the reaction to be complete, the solution was condensed by rotary evaporation (removing the CH_2Cl_2), leaving the blocked isocyanate behind.

The yield of blocked isocyanate was typically 95-100%.

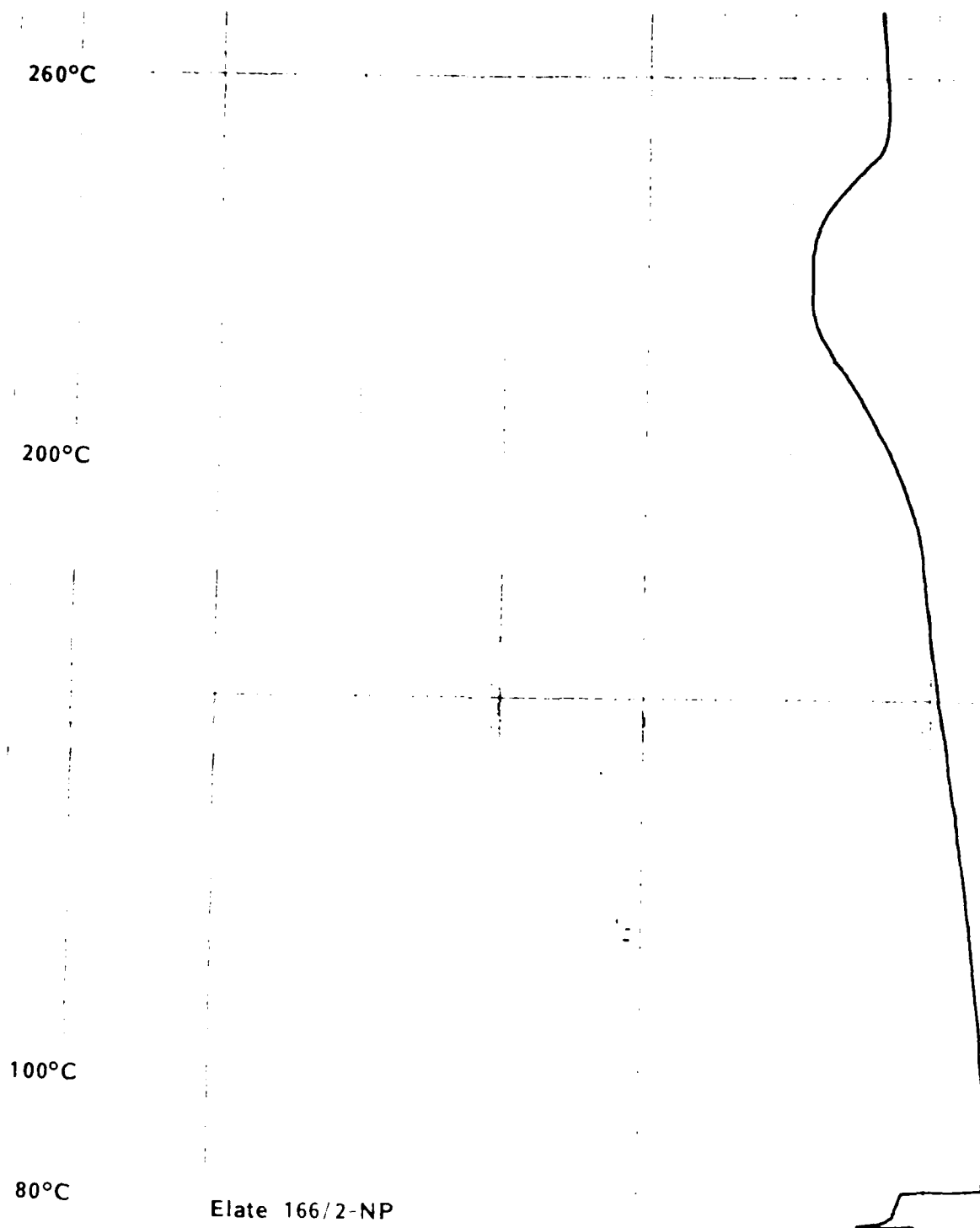
APPENDIX B

REPRESENTATIVE DSC TRACES



180°C

Elate 166/4 NP



160°C

140°C

120°C

100°C

80°C

Elate 160/2,4-DNP

160°C

140°C

120°C

100°C

80°C

TDI, 2-NP

180°C

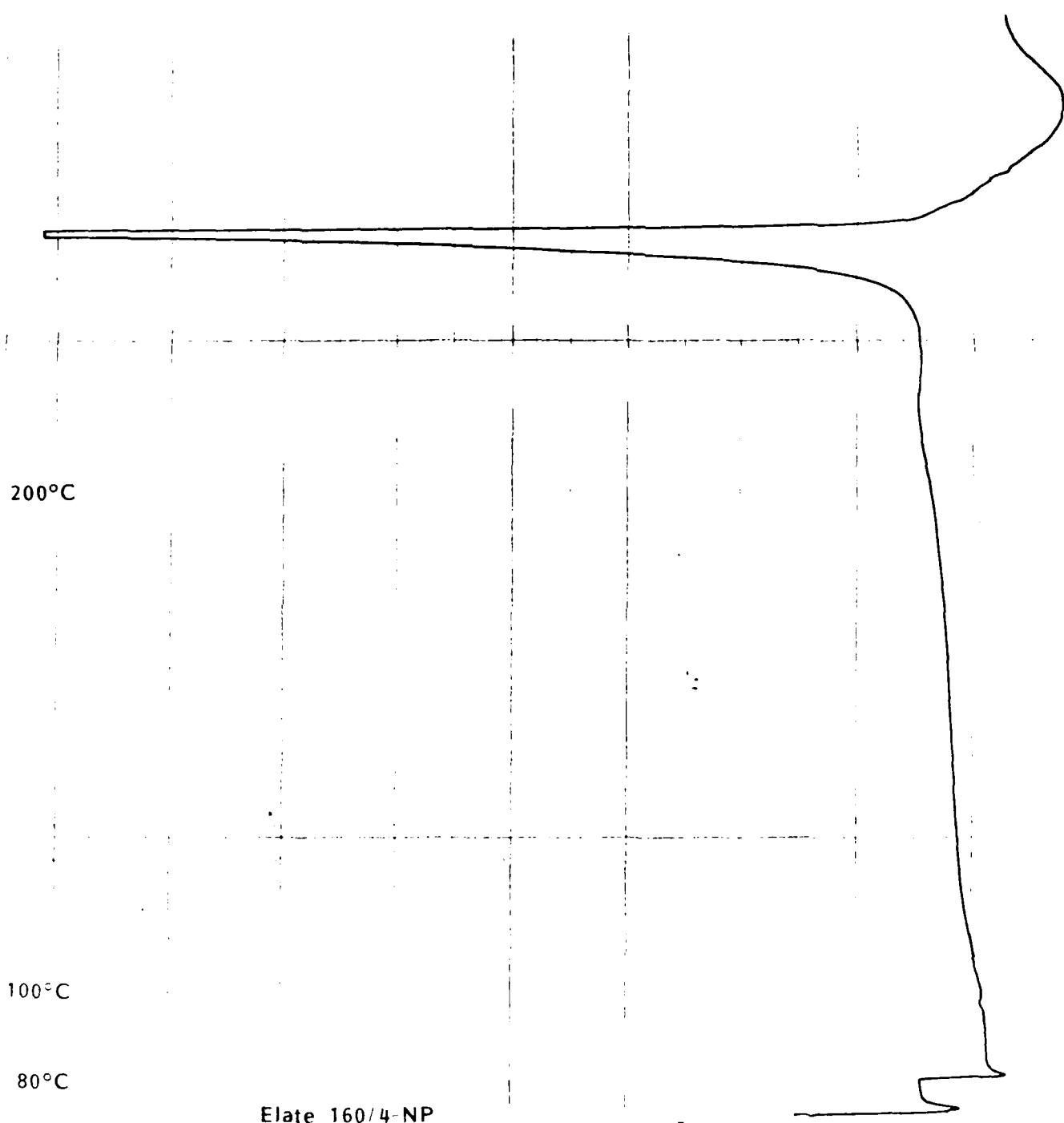
140°C

TDI/4-NP

80°C

20°C

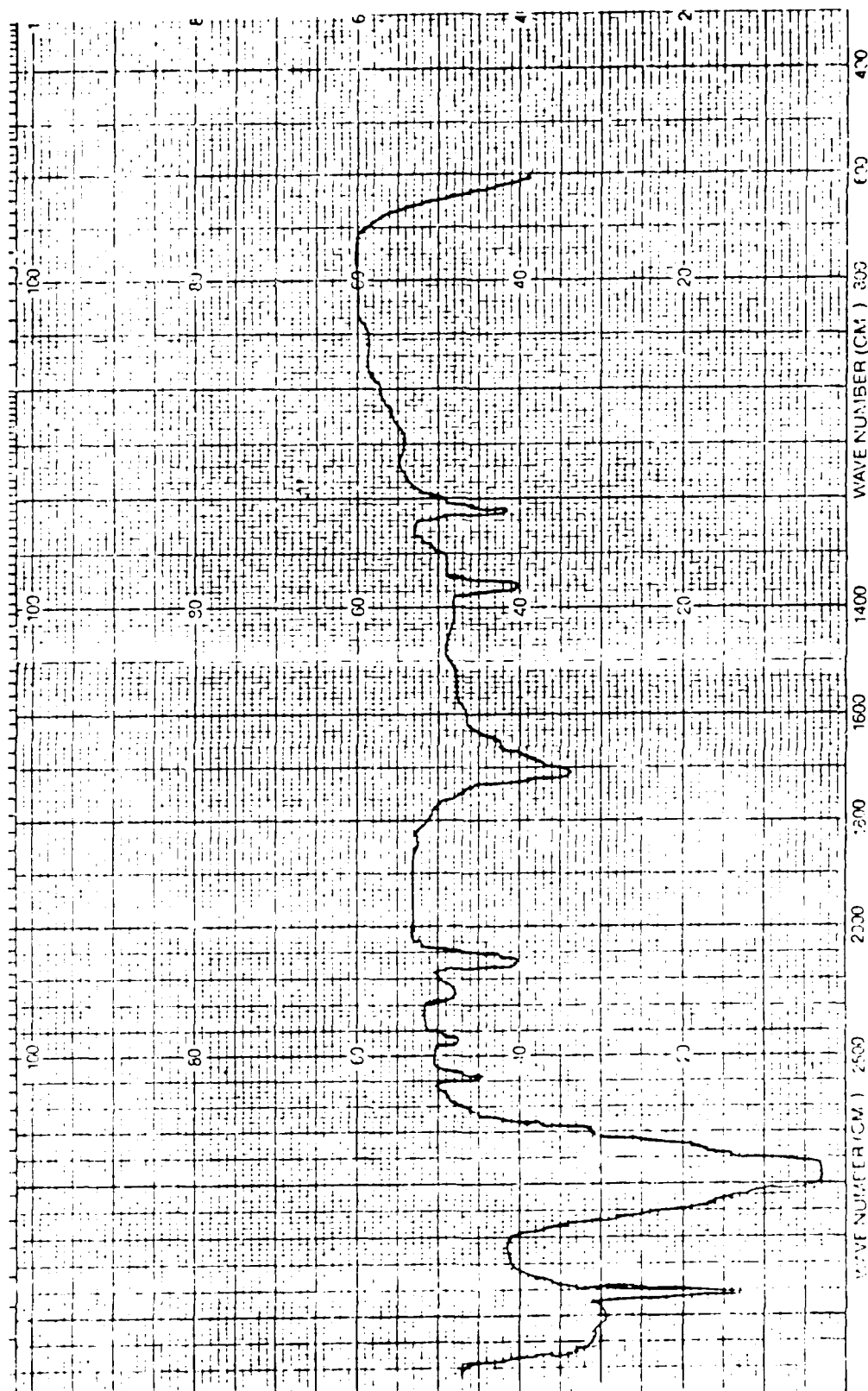
TDI/2,4-DNP



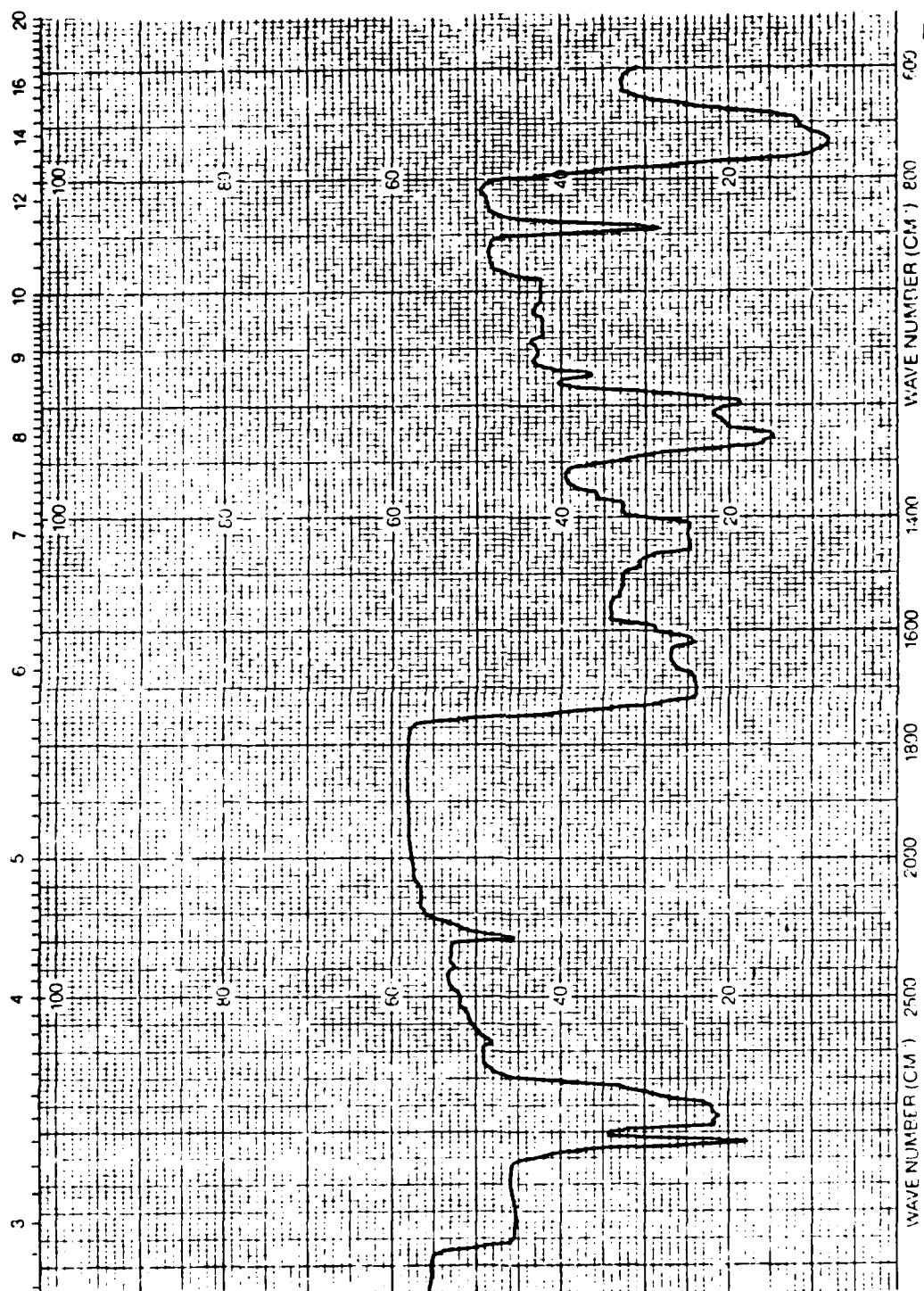
Elate 160/4-NP

APPENDIX C

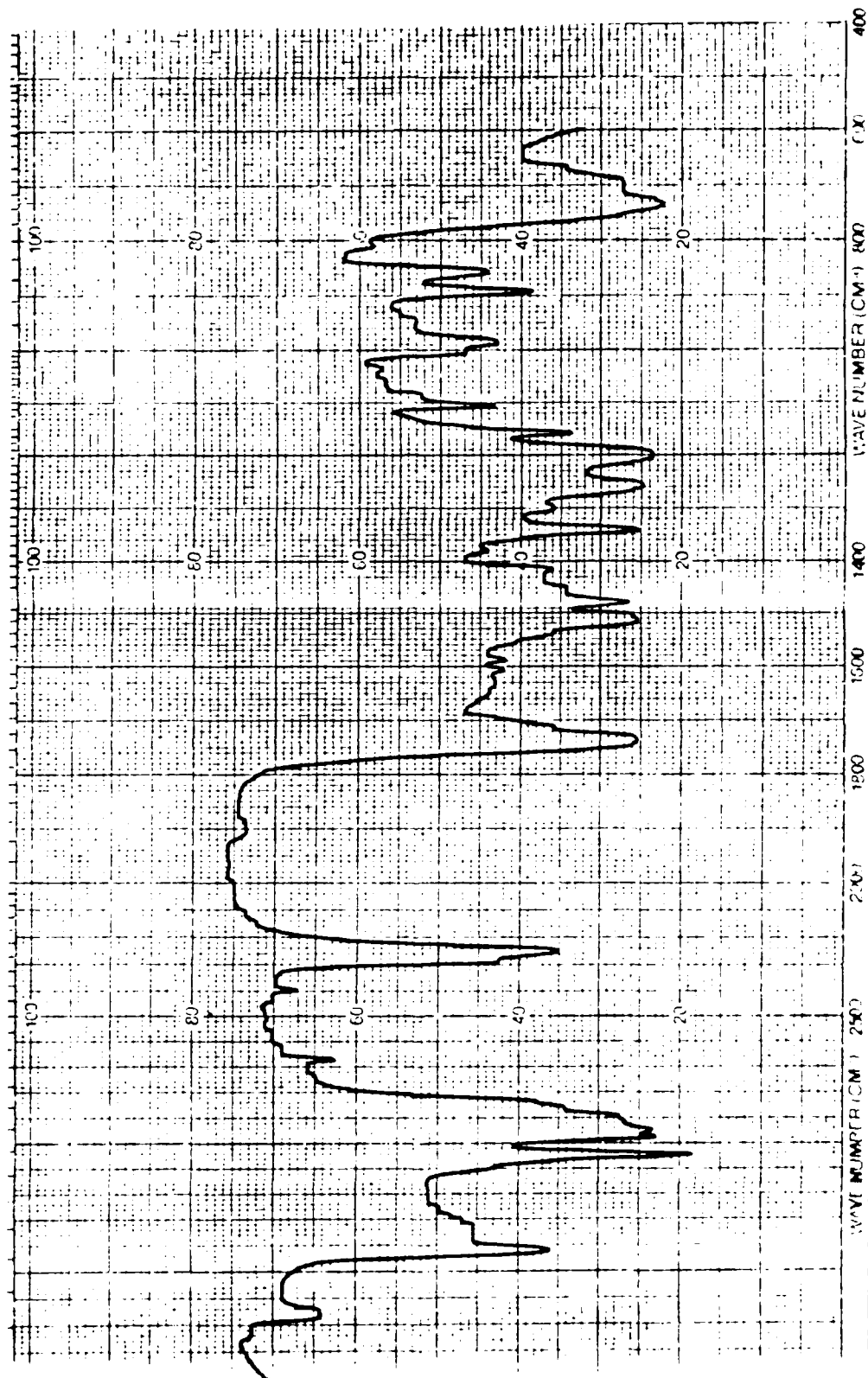
INFRARED SPECTRA OF
BLOCKED ISOCYANATES



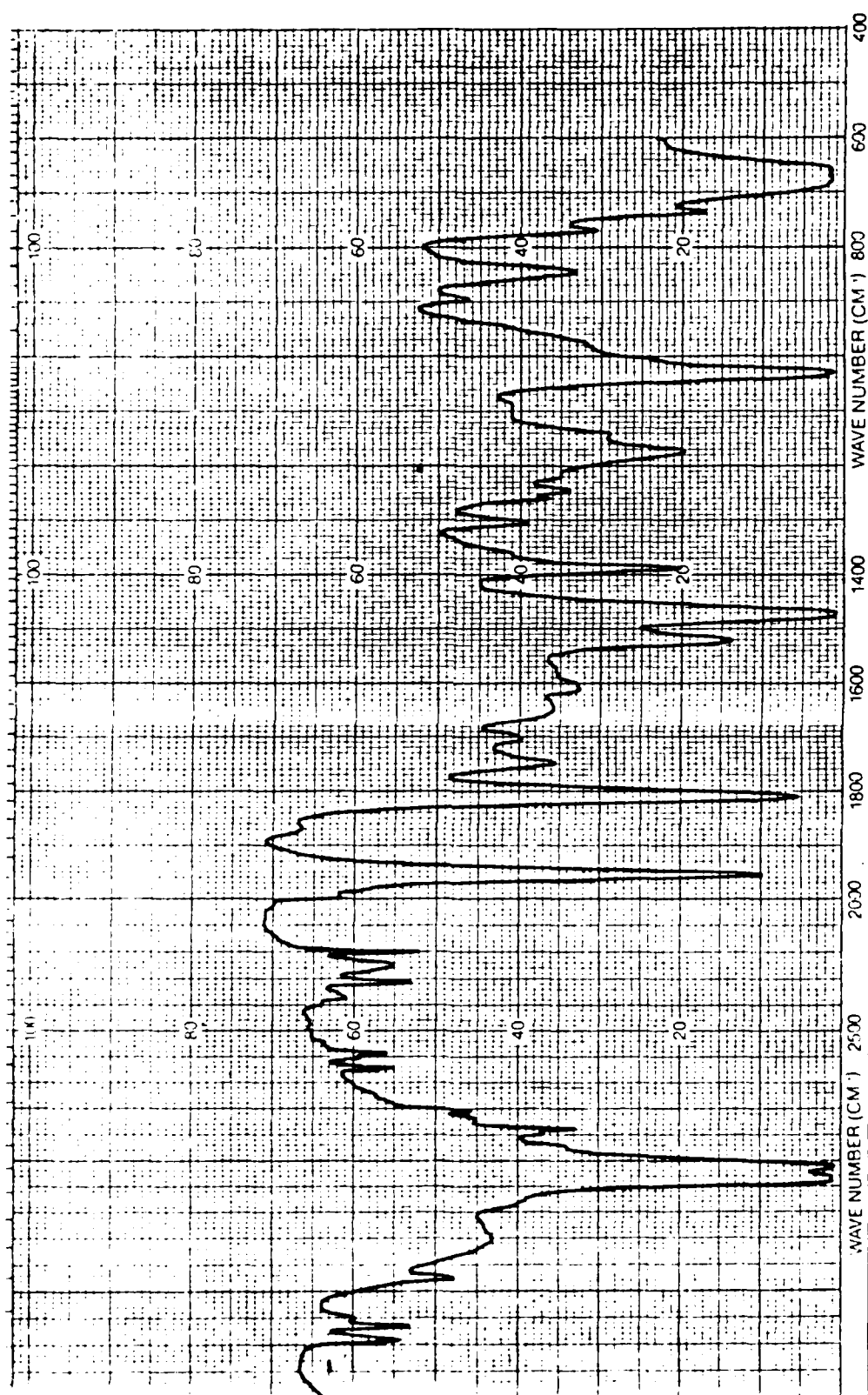
Infrared Spectrum of IPDI/MNA Run in Acetone.



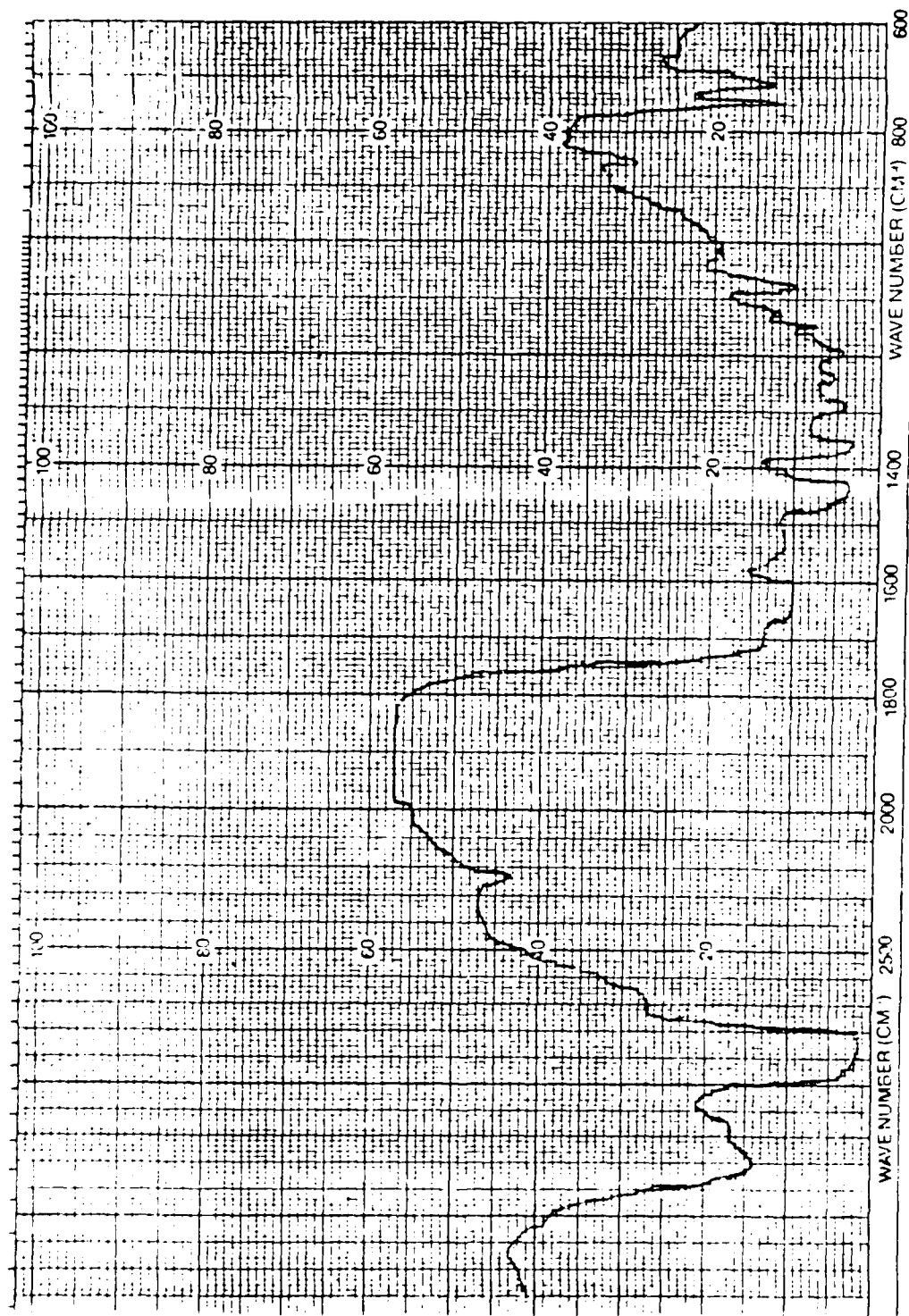
Infrared Spectrum of IPDI /Salicylaldehyde Run in CH_2Cl_2 .



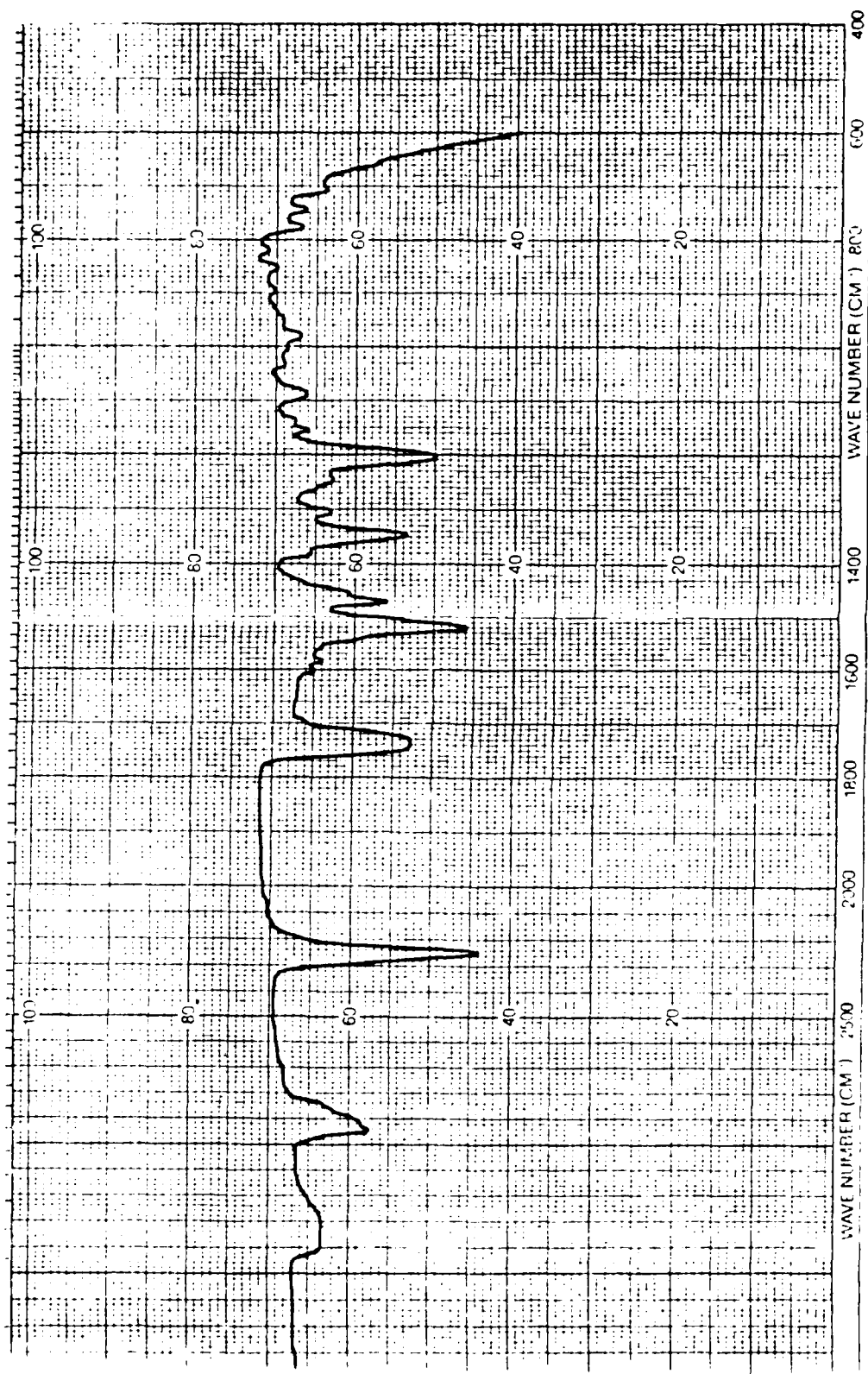
Infrared Spectrum of 4 NP/IPDI Run in CH_2Cl_2 .



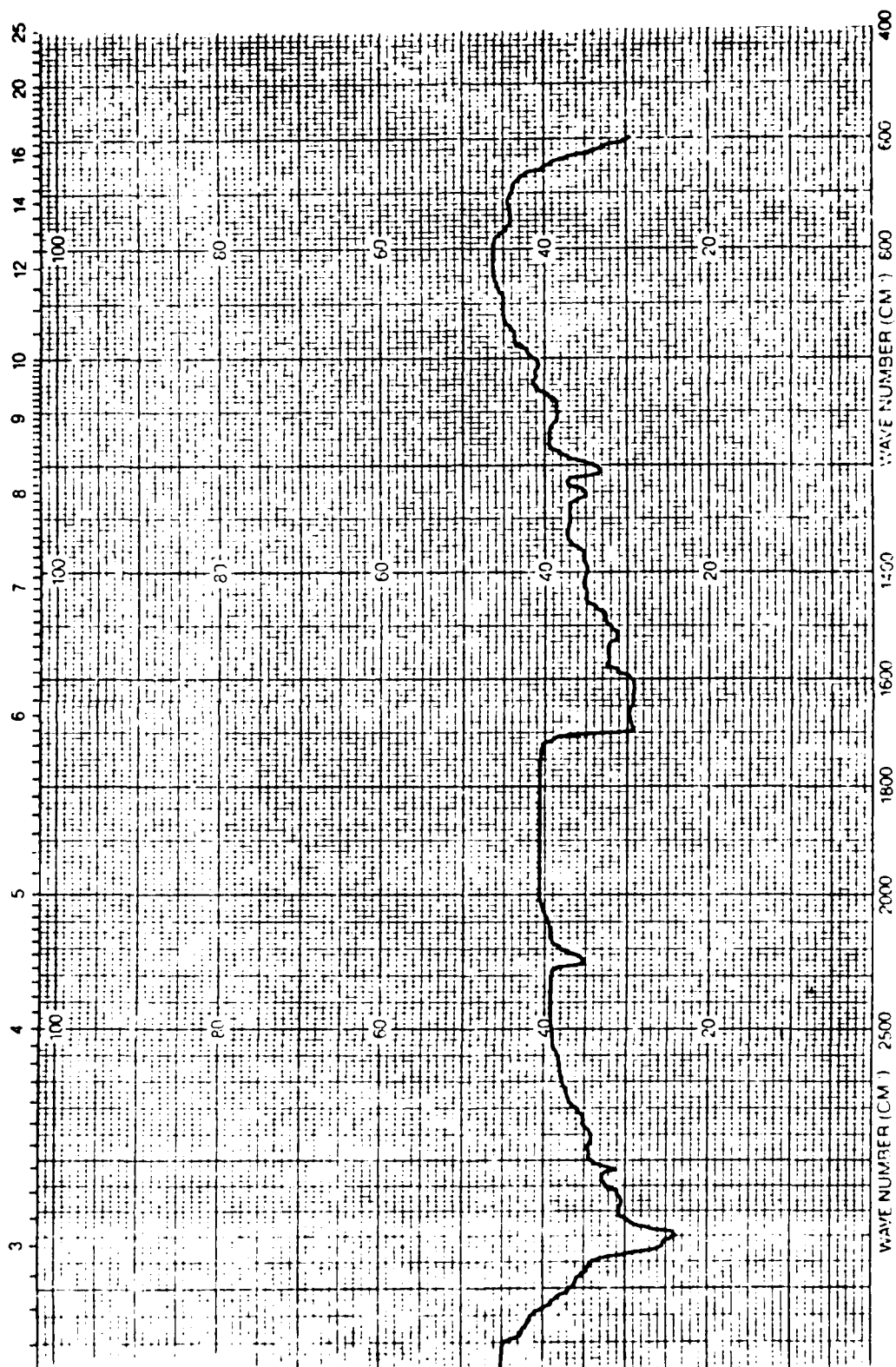
Infrared Spectrum of IPDI/Salicylamide Run in Benzene.



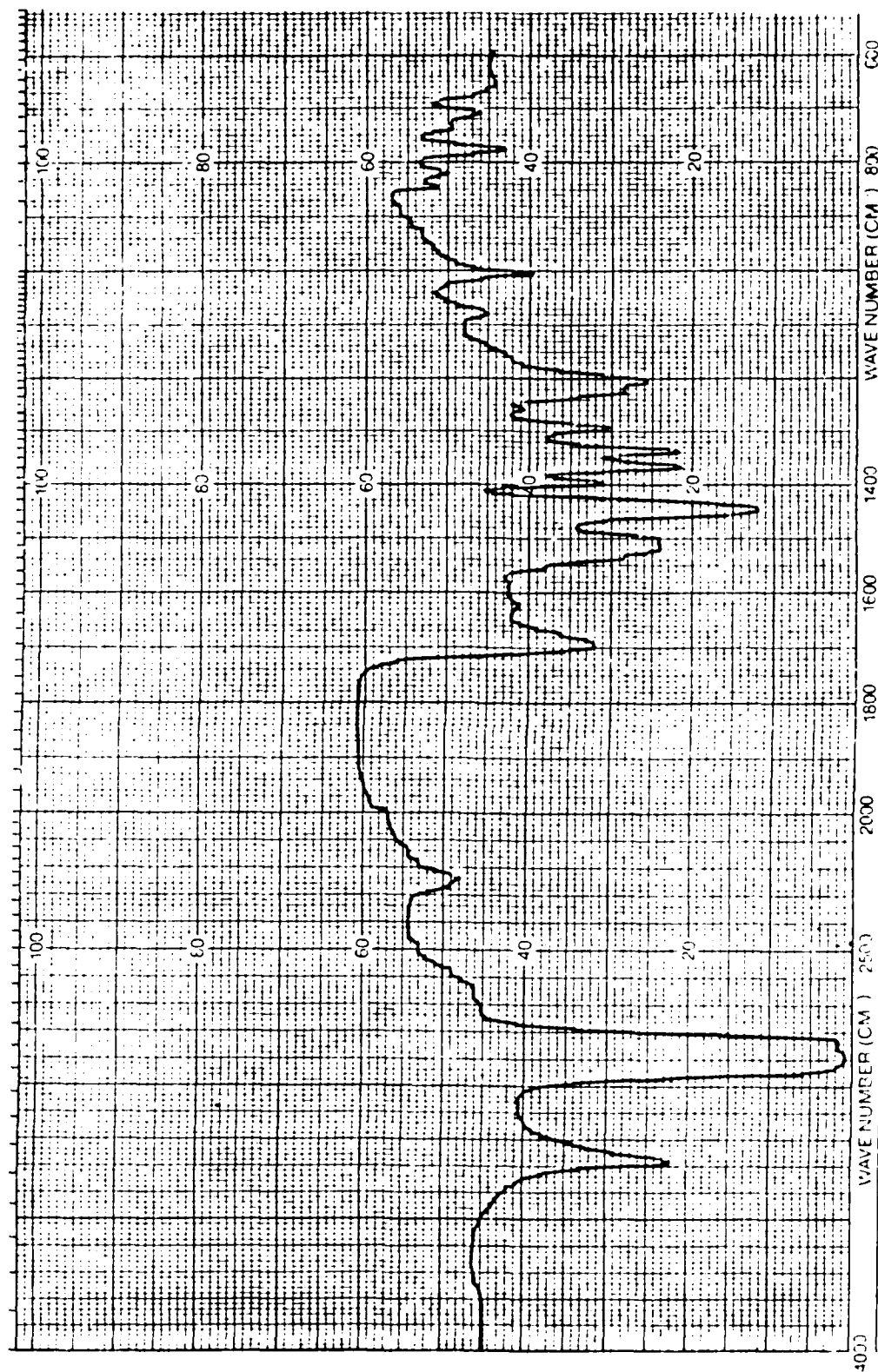
Infrared Spectrum of IPDI/Ethylsalicylate Run in Nujol Mull.



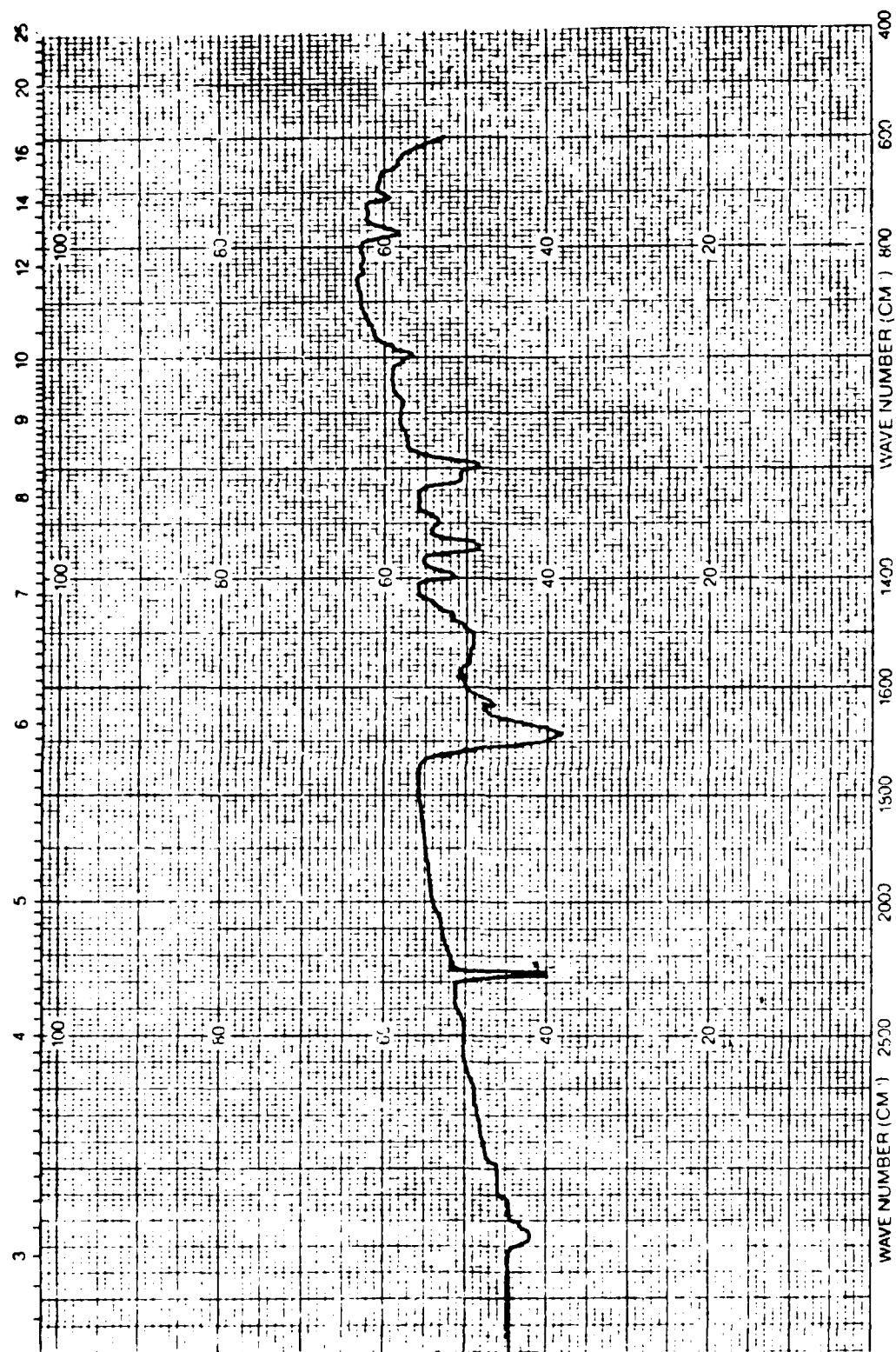
Infrared Spectrum of IPDI/2 NP Run in CH_2Cl_2 .



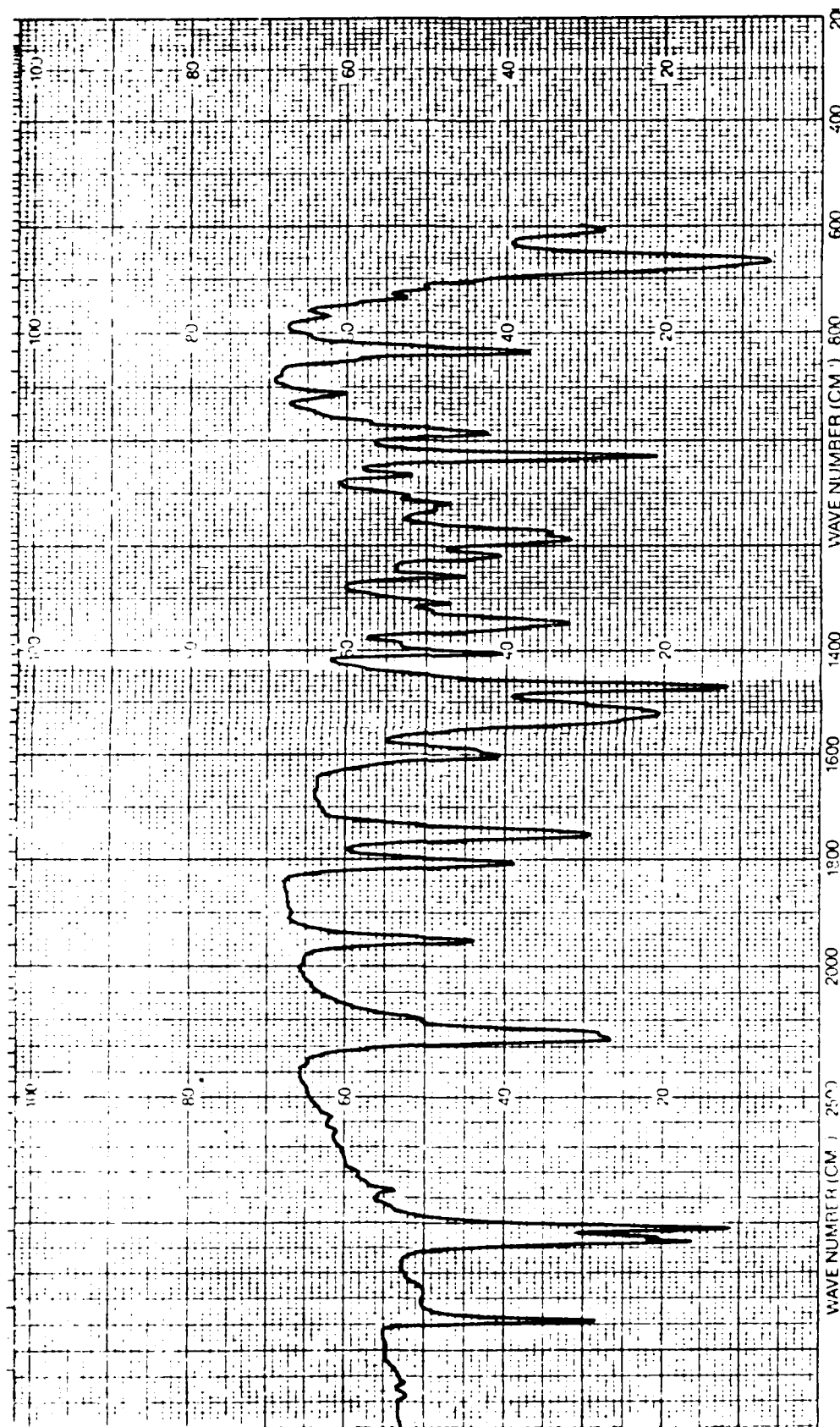
Infrared Spectrum of Elate 160/Salicylamide.



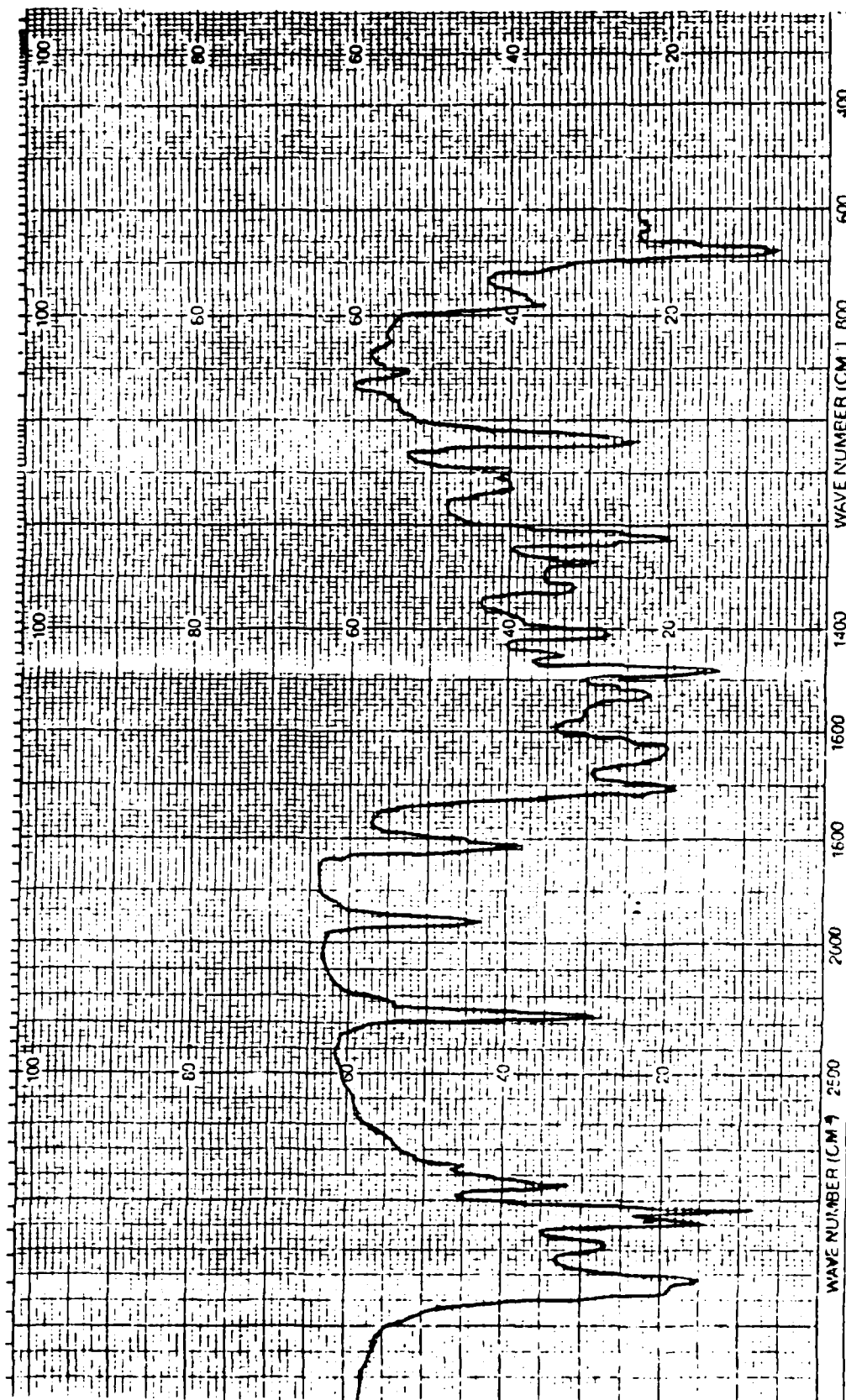
Infrared Spectrum of Elate 160/2 NP Run in Nujol Mull.



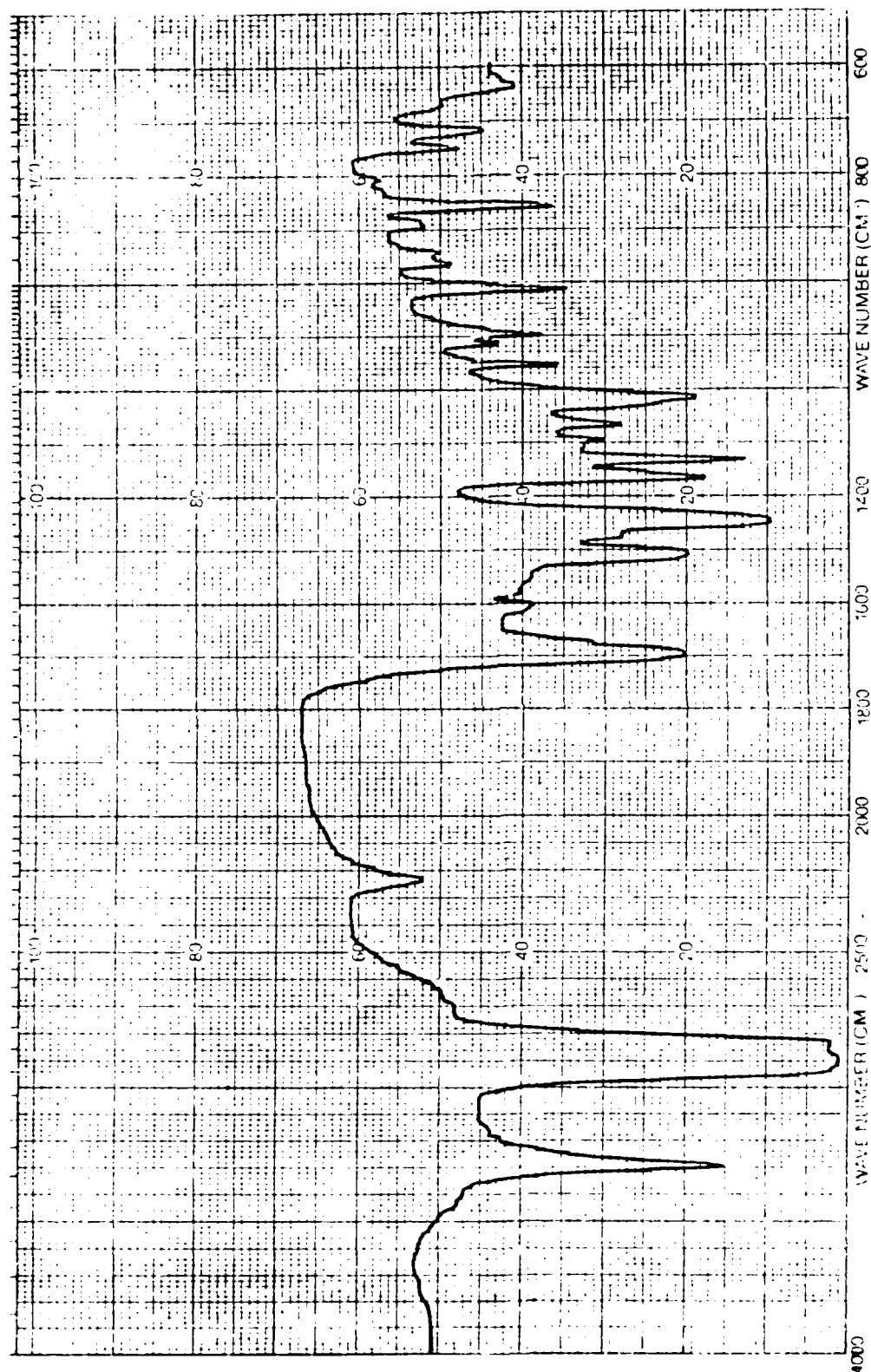
Infrared Spectrum of Elate 160/4-NP Run in CH_2Cl_2 .



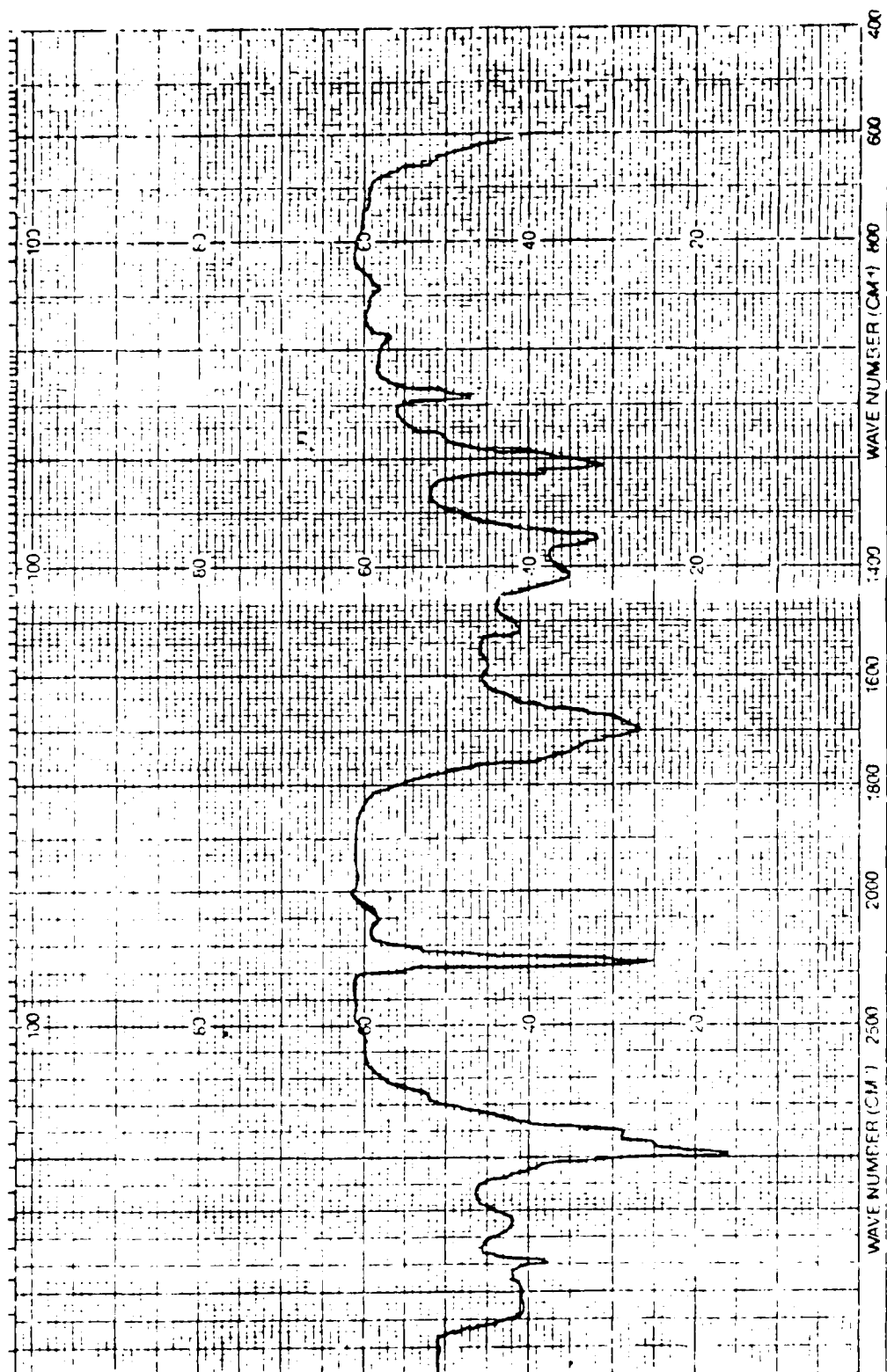
Infrared Spectrum of Elate 160/2, 4-DNP Run in Benzene.



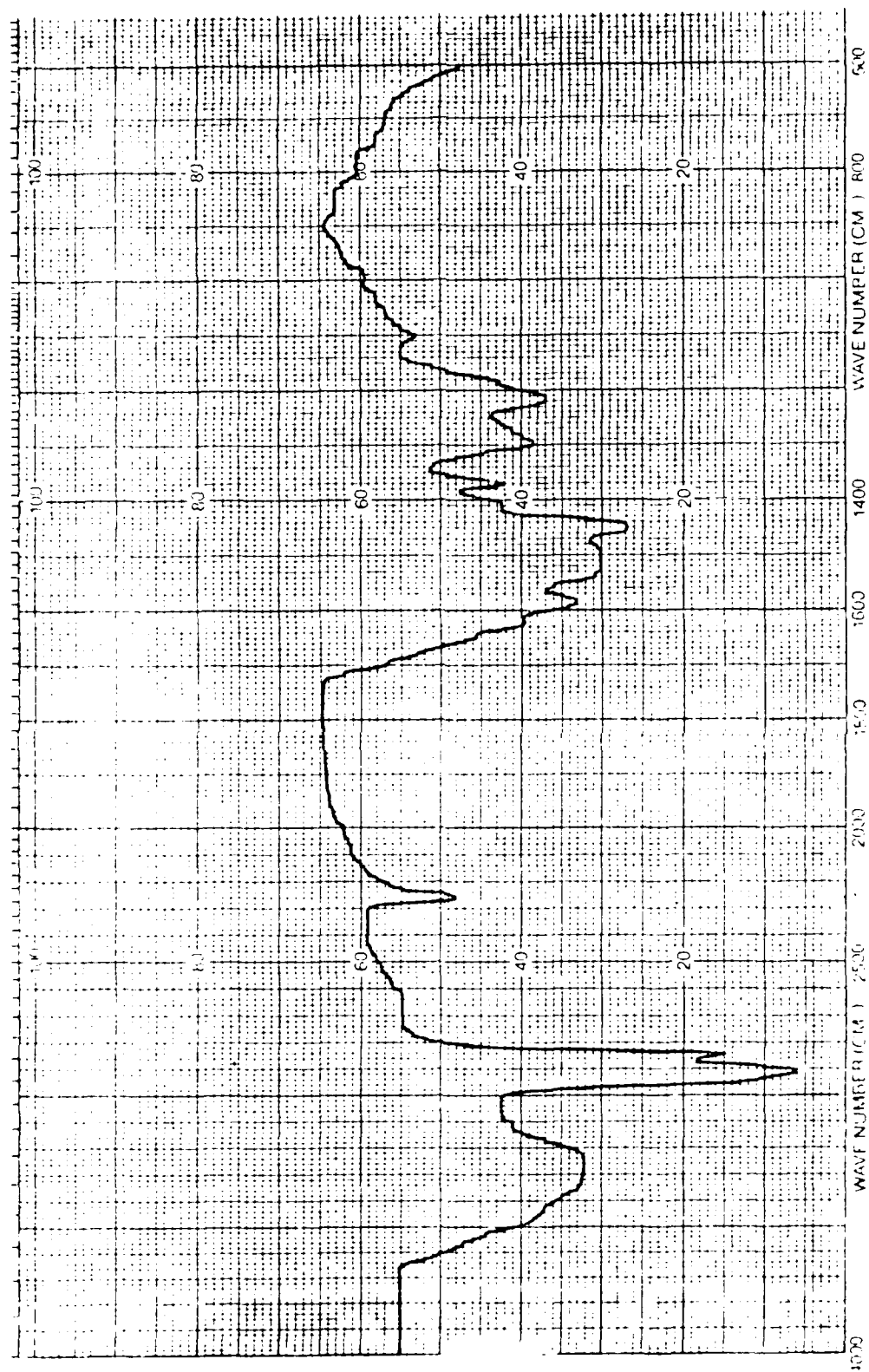
Infrared Spectrum of Elate 166/Salicylamide Run in Benzene.



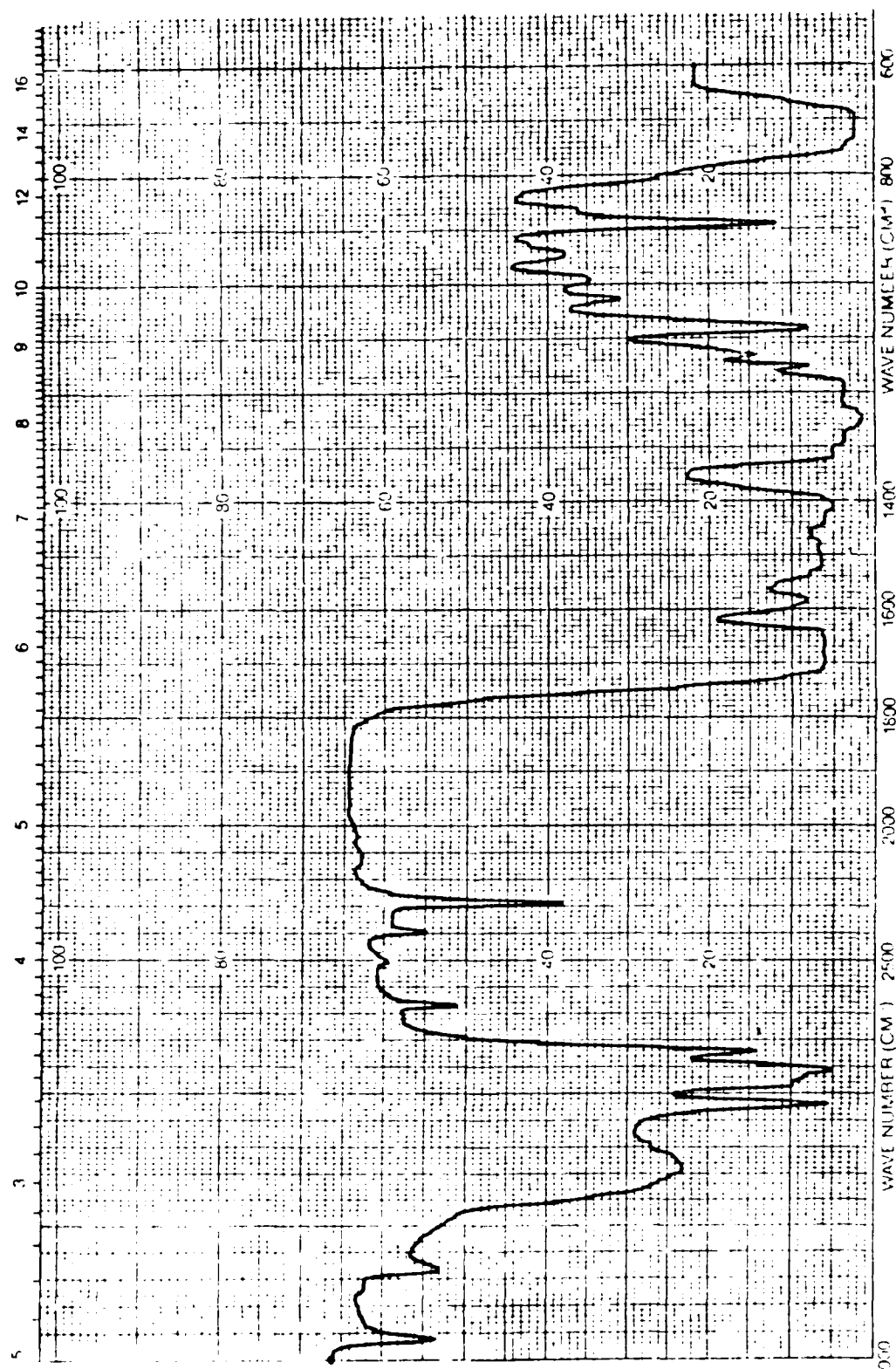
Infrared Spectrum of Elate 166/4-NP Run in Nujol Mull.



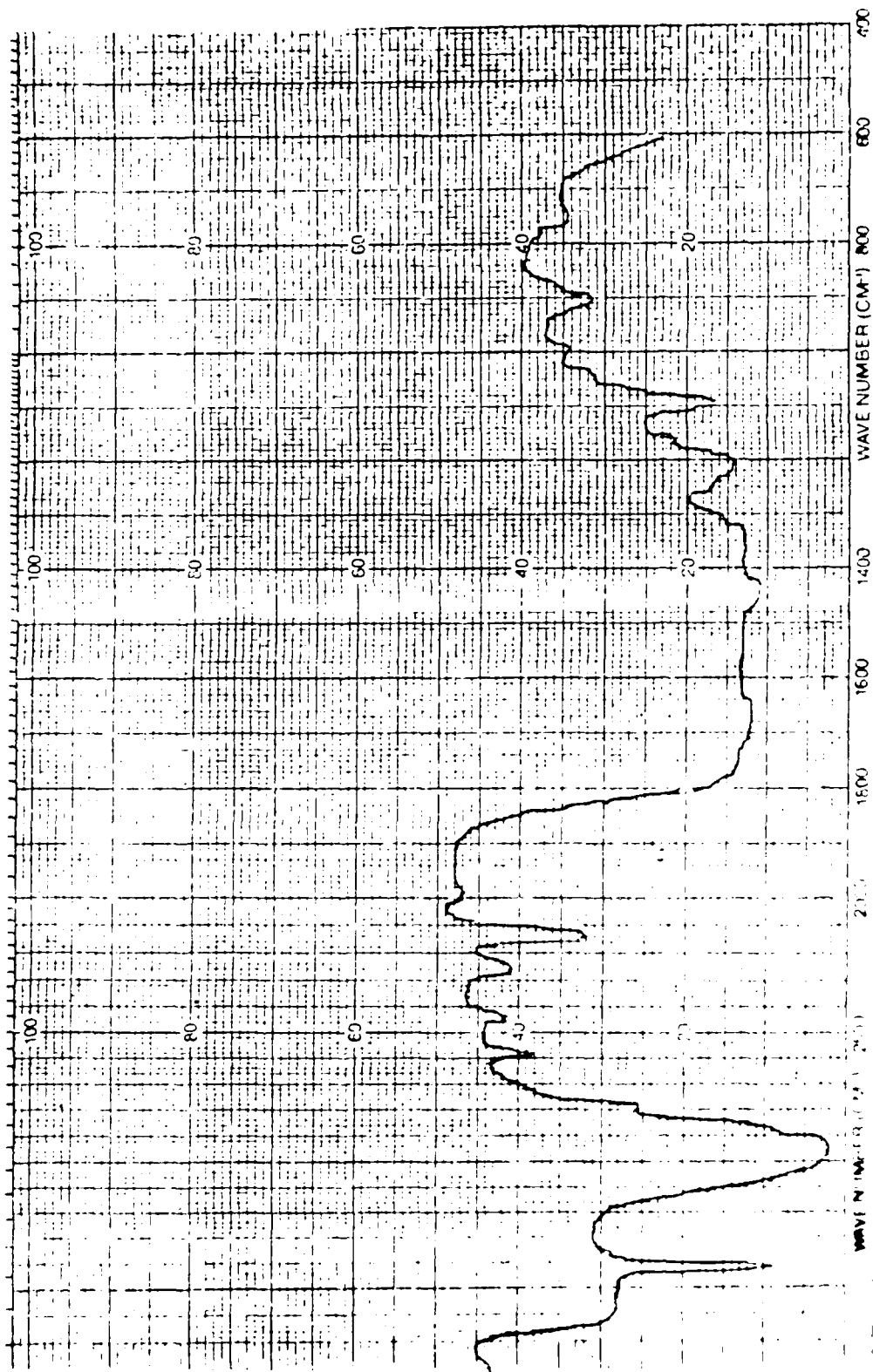
Infrared Spectrum of TDI/2-NP Run in Acetone.



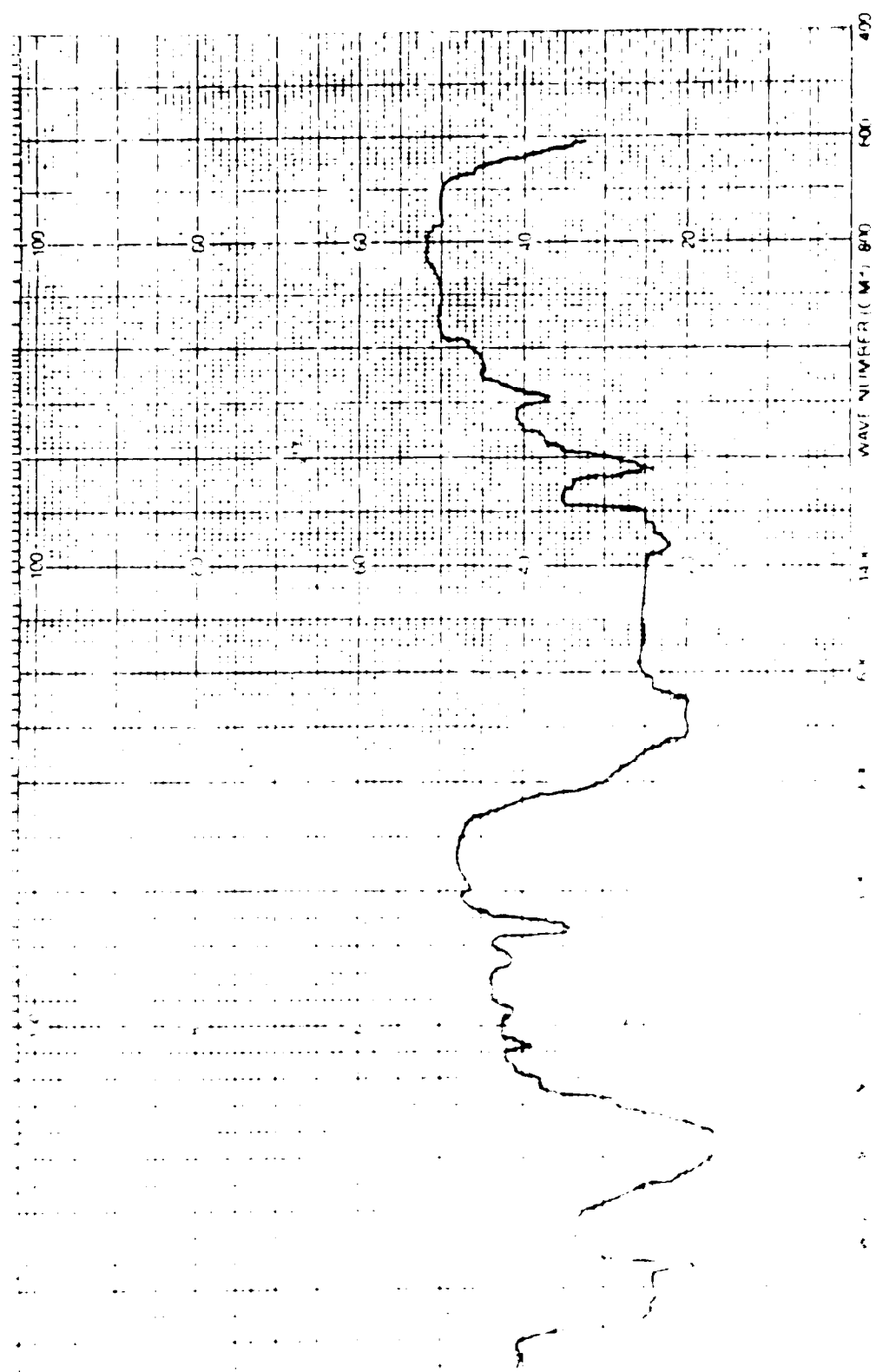
Infrared Spectrum of TDI/MNA Run in Nujol Mull.



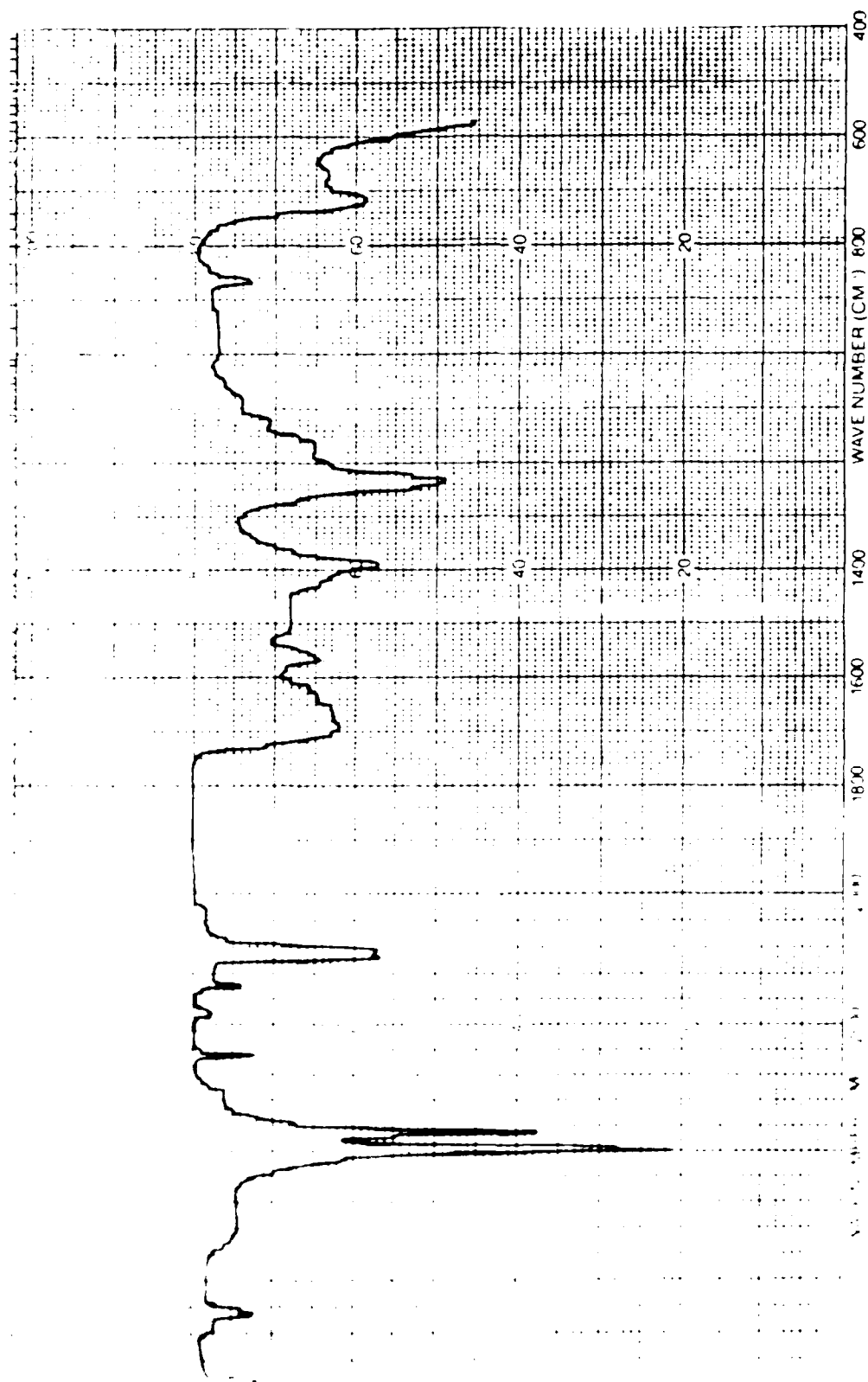
Infrared Spectrum of TDI/n Octylsalicylate Run in CH_2Cl_2 .



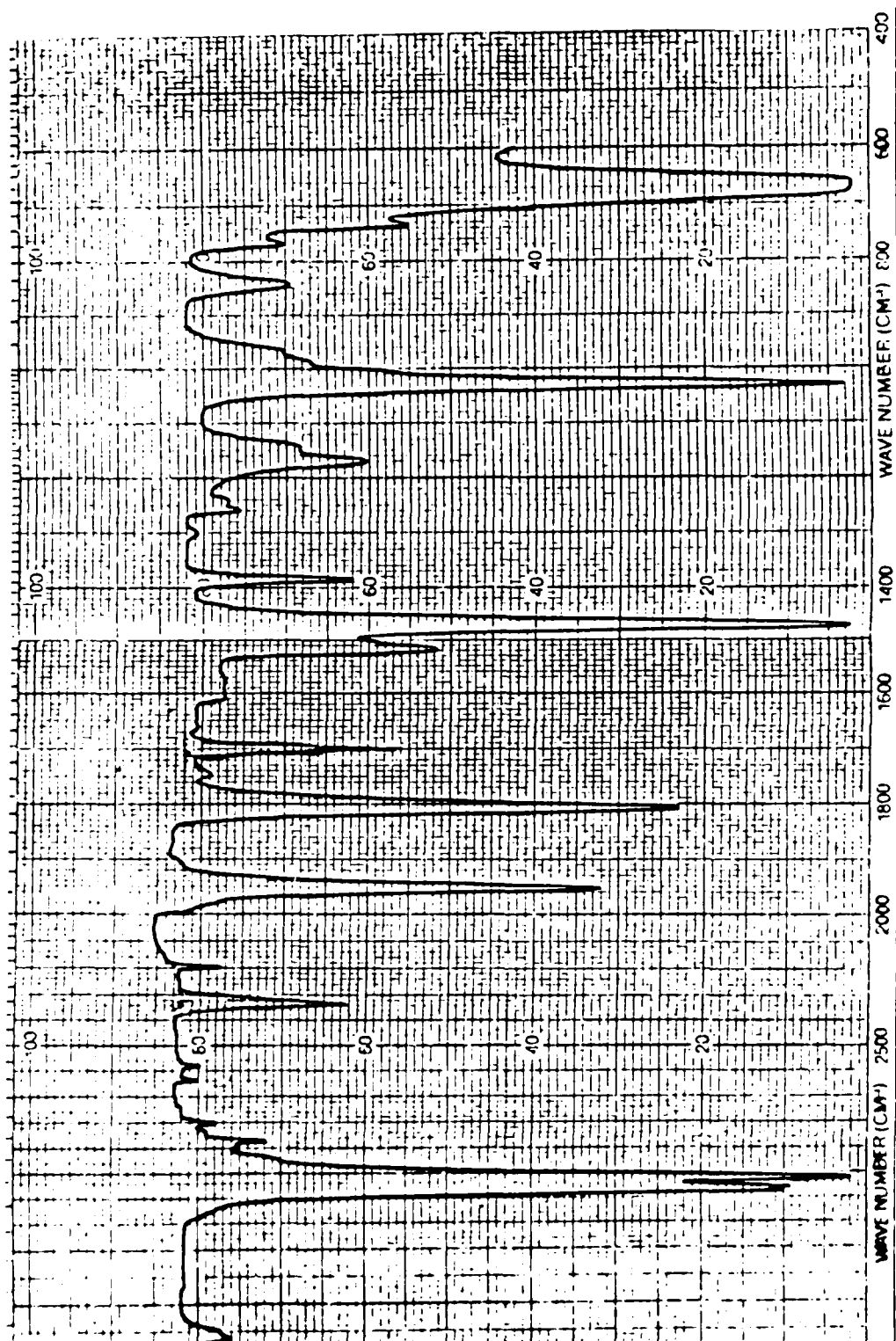
Infrared Spectrum of 2 Ethyl hexyl salicylate/TDI Run in Acetone.



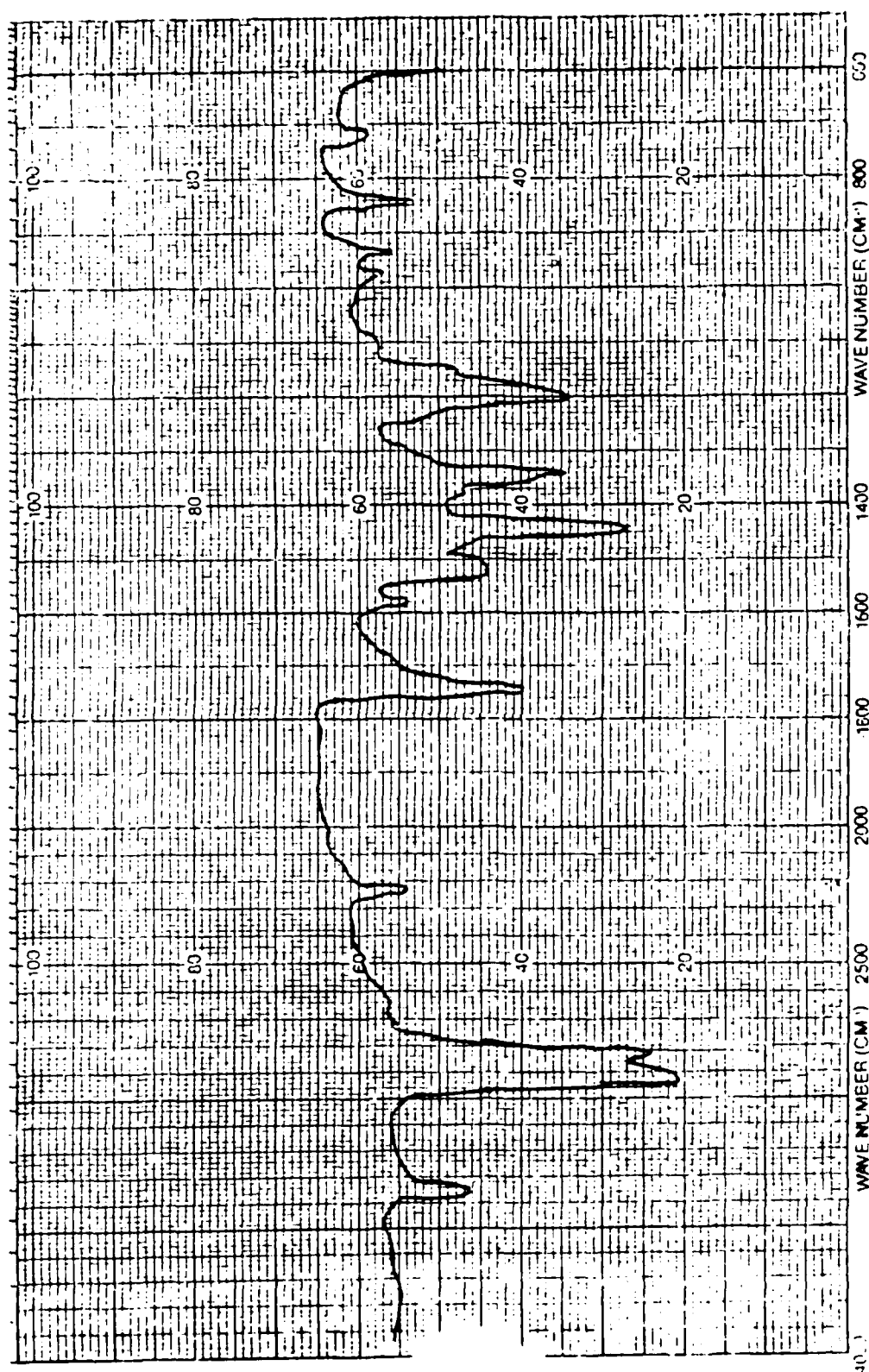
IR Spectrum of Diethyl Salicylate Run in Acetone.



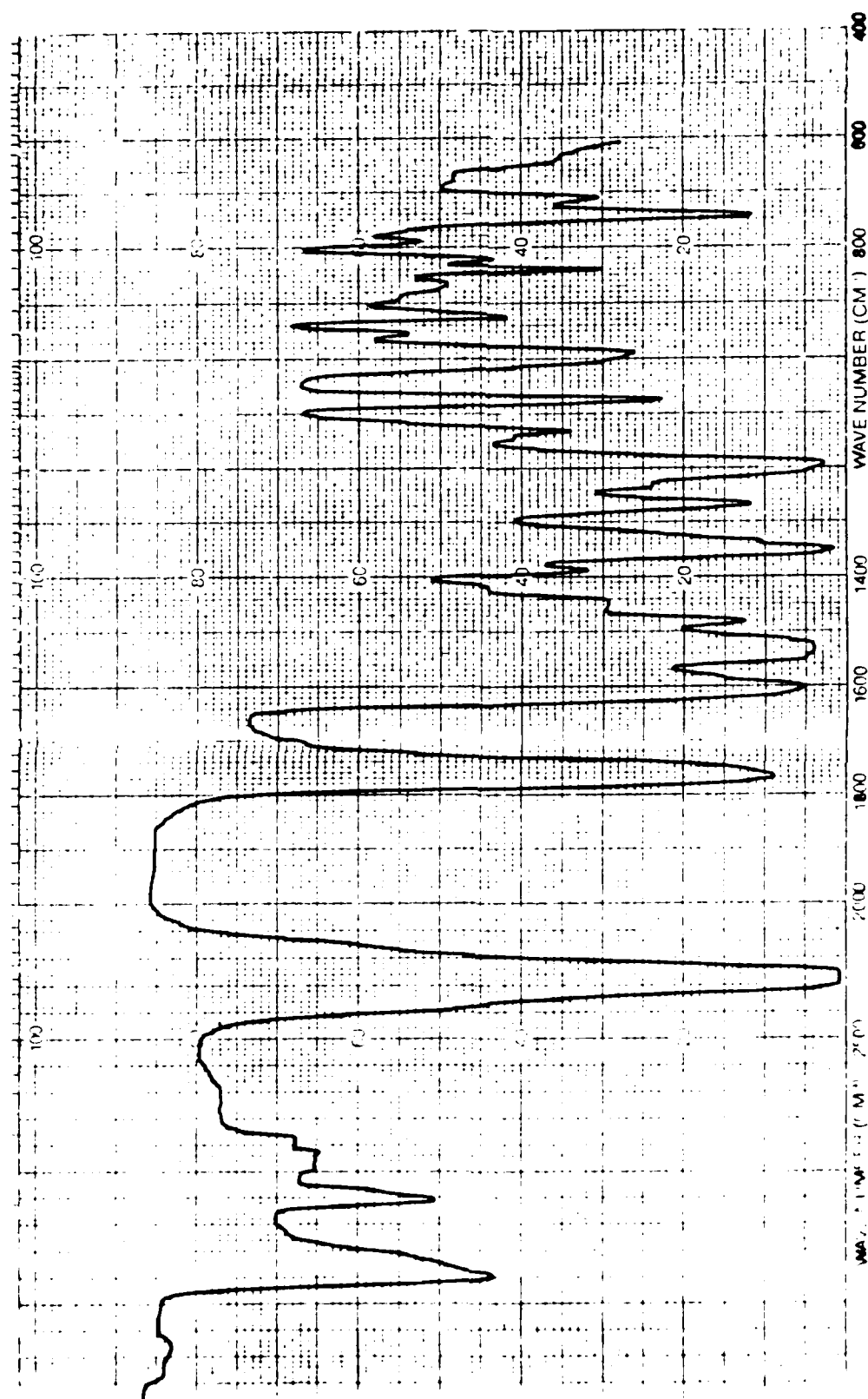
Infrared Spectrum of TDI Salicylaldehyde Run in CH_2Cl_2 .



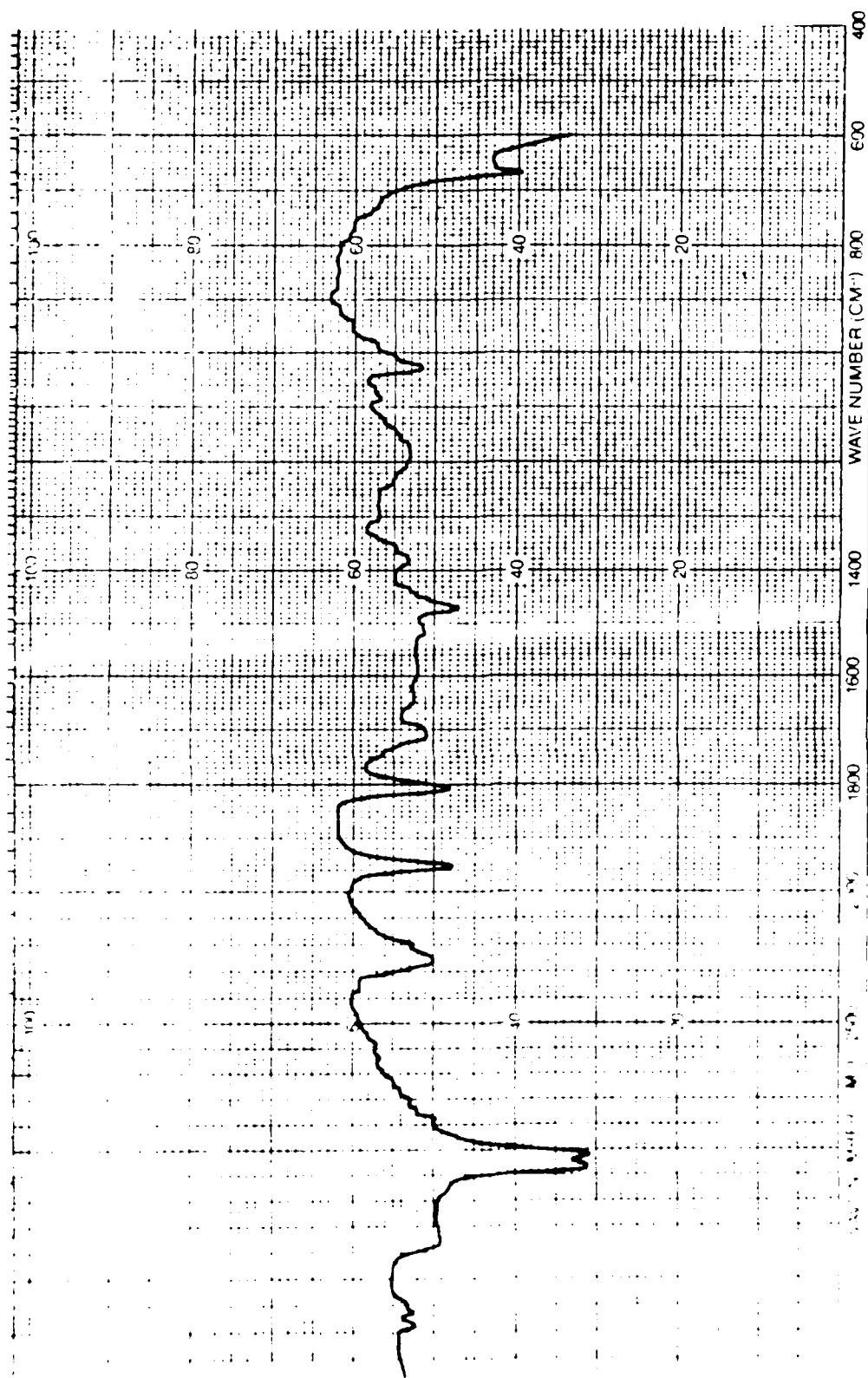
Infrared Spectrum of Elate 166/2 NP Run in Benzene.



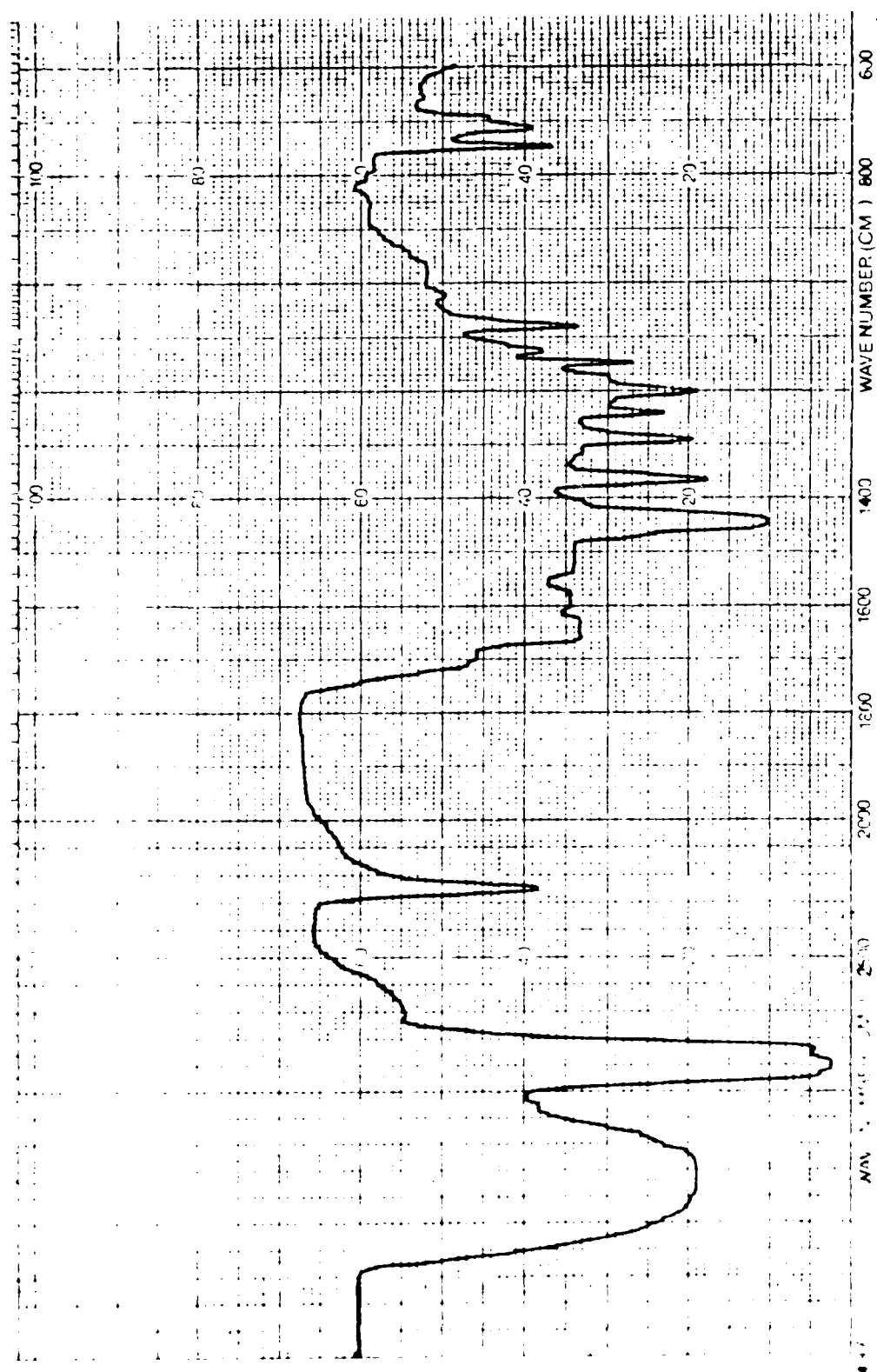
Infrared Spectrum of TDI/4-NP Run in Nujol Mull.



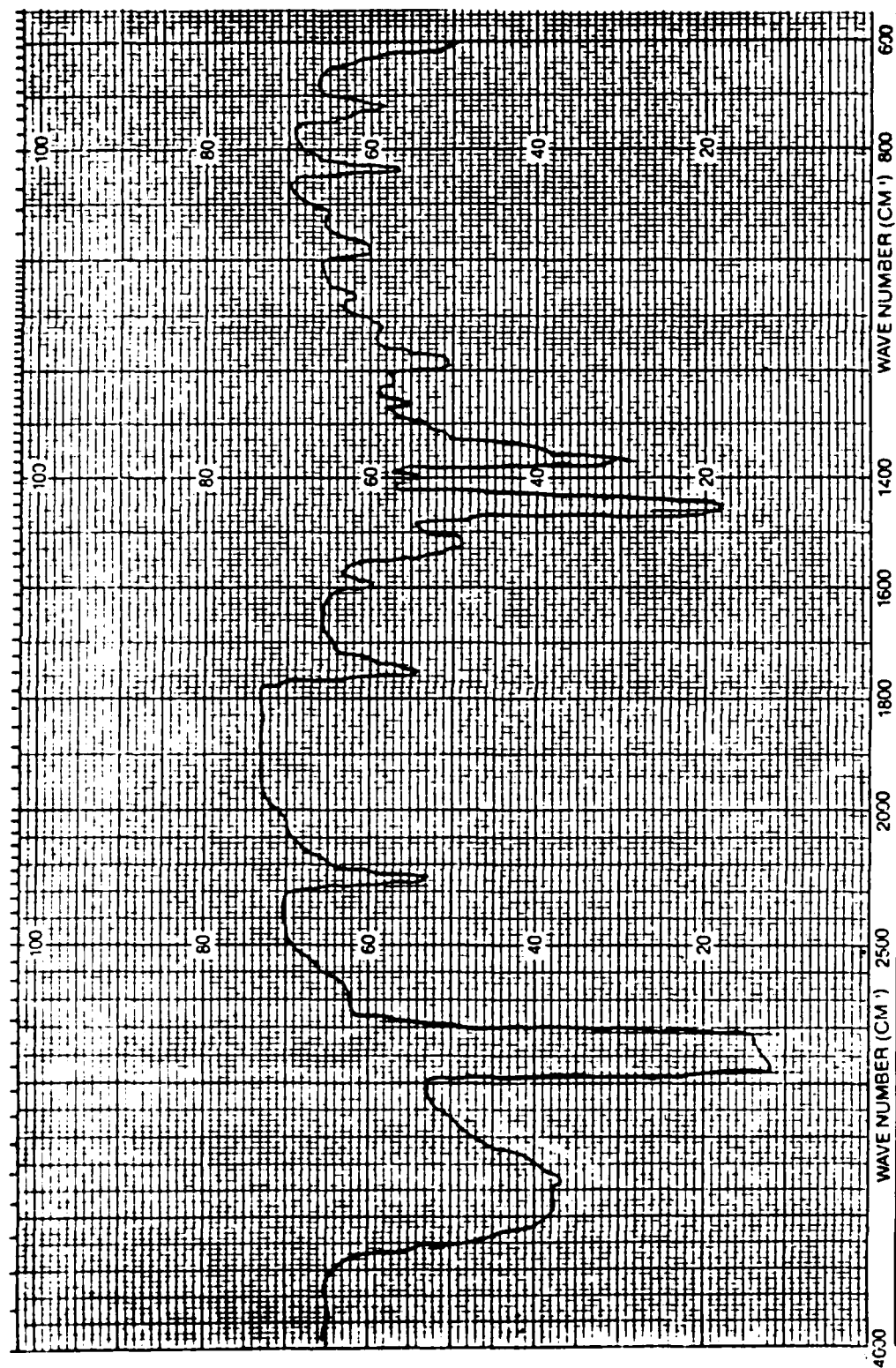
Infrared Spectrum of 2,4-DNP/TDI Run in CH_2Cl_2 .



Infrared Spectrum of TDI Salicylamide Run in Benzene.



Infrared Spectrum of TDI in Hexyl salicylate Run in Nujol Mull.



Infrared Spectrum of Elate 160/2,4-DNP Run in Nujol Mull.

APPENDIX D

NON-CARBON FULLED GUMSTOCKS

Gumstock A

PEG 4500	8 gram
Elate 160/2-NP	1 gram
Triacetin	5 gram
DBTDL	1 drop

Gumstock C

Elate 166/2,4-DNP	1 gram
R45M/AO	8 gram
DOA	5 gram
DBTDL	1 drop

Gumstock E

IPDI/MNA	1 gram
PEG 4500	8 gram
Triacetin	6 gram
DBTDL	1 drop

Gumstock G

TDI/2,4-DNP	1 gram
R45M/AO	8 gram
DOA	6 gram
DBTDL	1 drop

Gumstock B

TDI/4-NP	1 gram
R45M/AO	10 gram
Triacetin	5 gram
DBTDL	1 drop

Gumstock D

TDI/2-NP	1 gram
R45M/AO	8 gram
DOA	5 gram
DBTDL	1 drop

Gumstock F

Elate 160/2,4-DNP	1 gram
R45M/AO	8 gram
DOA	5 gram
DBTDL	1 drop

APPENDIX E

CARBON FILLED GUMSTOCKS

Gumstock A

Elate 160/2-NP	1 gram
R45M/AO	3 gram
DOA	4 gram
Carbon	0.4 gram
DBTDL	1 drop

Gumstock C

TDI/2-NP	1 gram
R45M/AO	3 gram
DOA	4 gram
Carbon	0.4 gram
DBTDL	1 drop

Gumstock E

TDI/2,4-DNP	1 gram
R45M/AO	3 gram
DOA	5 gram
Carbon	0.4 gram
DBTDL	1 drop

Gumstock B

TDI/4-NP	1 gram
R45M/AO	3 gram
DOA	5 gram
Carbon	0.4 gram
DBTDL	1 drop

Gumstock D

Elate 160/2,4 DNP	1 gram
R45M/AO	3 gram
DOA	4 gram
Carbon	0.4 gram
DBTDL	1 drop

END

3-87

DTIC